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Birmingham, AL

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Final Report

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SECTION 1

INTRODUCTION

The increasing use of sulfur-bearing coal for the production of electrical energy, the generation of significant quantities of sulfuric acid aerosol by catalytic converters in automobiles, and the appearance of new information on the irritant effects of sulfuric acid and sulfates are factors that have combined to intensify interest in the measurement of ambient sulfuric acid aerosol. The emission of sulfuric acid by automobiles is a problem of special interest because of the fairly high concentrations found in the immediate vicinity of roadways and the small size of the sulfuric acid particles generated.

In a series of measurements made with catalyst-equipped automobiles at the General Motors Test Track in October, 1975, it was found that most of the sulfur in gasoline was oxidized to sulfur trioxide and appeared as sulfuric acid aerosol near the test site. Concentrations in the range of 3 to 6 $\mu g/m^3$ were found. The sulfuric acid was apparently neutralized or partially neutralized by ambient ammonia within a fairly short time and within a fairly short distance of travel. Nevertheless, the possible harmful effect on the health of persons in the vicinity of heavily traveled roadways continues to be a matter of serious concern.

The potentially harmful health effects stem from certain unique properties of sulfuric acid aerosol. Sulfuric acid is the most severe bronchial and lung irritant among the various species of sulfur compounds that can occur in the atmosphere. The particles derived from automobiles have a mass mean diameter of only a few hundredths of a micrometer and therefore can penetrate deeply into the lung and be deposited in the alveoli. These small particles are relatively highly concentrated in terms of the molarity of the sulfuric acid and are therefore stronger irritants than particles that have grown in size over a period of time by coagulation and adsorption of water vapor.

In order to assess the health effects potential of sulfuric acid having the properties described, it is necessary to have sampling and analytical methods that will measure sulfuric acid concentrations without interference or artifacts arising from the presence of other substances in the sampled atmosphere or from various environmental factors such as relative humidity or temperature. Because many interfering reactions are possible, especially during the collection of a sample, the accurate determination of sulfuric acid aerosol is a difficult problem that is just now beginning to be adequately solved.

Although sampling cannot be arbitrarily isolated from the method of analysis subsequently used to determine the species sought, there are certain difficulties peculiar to sampling sulfuric acid aerosol. In general terms, these difficulties may be said to result from interactions of sulfuric acid with other particulate and gaseous constituents of the ambient atmosphere or the sample and from the simultaneous presence in the atmosphere of sulfate salts and sulfur dioxide. Reactions of sulfuric acid with copollutants have been shown to occur on filters, the collection medium that is generally best suited for sampling atmospheric particulate material. The oxidation of sulfur dioxide to sulfate also occurs on filters under certain conditions. These phenomena—and others that may be expected to occur—often result in failure of attempts to measure ambient concentrations of sulfuric acid because some or all of the acid is lost during the sampling process. Furthermore, methods of analysis that involve dissolving the sulfuric acid along with other soluble constituents of the sample introduce errors resulting from reactions that occur in the solvent medium; a sampling method that will permit subsequent processing and analysis of the sample without loss (or addition) of sulfuric acid is therefore desirable.

Work on this contract was concerned principally with providing a sampling and analytical method that will avoid errors resulting from degradation of sulfuric acid during or after its collection on a filter. During the early months of the contract period, efforts were made to evaluate the collection of sulfuric acid aerosol and effects of interferents using flame photometric detection. However, it was later concluded that the fixation of sulfuric acid as a stable, nonreactive product is clearly a desirable approach, and may well provide the only means of avoiding interference effects.

This Final Report describes the techniques used to generate the sulfuric acid aerosol, the analytical methods used to measure sulfuric acid, and the prototype apparatus and procedures for derivatization of sulfuric acid both as the aerosol and as the prefiltered vapor. Further, it gives the results of laboratory experiments designed to determine the effects of various potential interferents on the collection of sulfuric acid, the results of field sampling with a prototype sampler, and a summary of the conclusions reached.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The collection of sulfuric acid aerosol on Teflon filters, as a first step in the measurement of ambient sulfuric acid concentrations, is subject to interference by alkaline gases and by particulate material in the air sample. Substantial losses of sulfuric acid are caused by gaseous ammonia and ambient particulate material from an urban environment. Since the determination of atmospheric sulfuric acid aerosol collected on a filter over a period of time is subject to error from interfering reactions that may occur during sampling, the need is evident for stabilization of sulfuric acid during sampling. Direct methods of fixation of sulfuric acid aerosol were not found to be selective; it appeared that a better method of sampling would involve selective volatilization of the sulfuric acid and filtration of the ambient particulate interferents prior to derivatization of the vapor.

A prototype sampler—based on the concept of volatilization, prefiltration, and derivatization of sulfuric acid—was constructed and demonstrated to be of practical value for determination of ambient sulfuric acid aerosols in both laboratory and field studies. This methodology in conjunction with sulfate determinations by ion chromatography has the following advantages:

- Minimal losses of sulfuric acid during sampling—less than 15%.
- Good specificity—freedom from the usual sources of interference in determinations of sulfuric acid, i.e., other sulfur species.
- Good sensitivity—with a conservative limit of detection of 0.5 μg of sulfuric acid per cubic meter of ambient air.
- Excellent stability of collected samples for IC analysis in the laboratory at a later date.

The following recommendations would provide a logical extension of this work:

- Further improve the conditions and apparatus for volatilization and prefiltration of sulfuric acid, emphasizing the effects of volatilization temperature, sampling flow rate, and nature of exposed surfaces within the sampling device.
- Conduct a systematic evaluation of other derivatizing agents and filter media impregnated with the derivatizing agents to achieve optimal fixation of the volatilized sulfuric acid so that the derivative can be readily identified and quantitated.
- Investigate in depth the potential for interference from ambient gaseous compounds and ambient particulate material, especially various size aerosols of ammonium sulfate salts, during sampling of sulfuric acid aerosol with the combined volatilization, prefiltration, and derivatization methodology.

SECTION 3

SUMMARY OF RESULTS

The most significant results of the experimental studies conducted during this contract are summarized in the following paragraphs. Details are given in the latter sections.

RESULTS OF INTERFERENCE STUDIES WITH SULFURIC ACID COLLECTED ON FILTERS

- Sulfuric acid aerosol was collected on Teflon filters with predeposited Fe_2O_3. Average recoveries of sulfuric acid samples were 18% for "high" levels and 79% for "low" levels of Fe_2O_3, as measured by flame photometric detection (FPD) at 200°C.

- Sulfuric acid aerosol was collected on Teflon filters with predeposited PbO. Average recoveries of sulfuric acid samples were 19% for "high" levels and 66% for "low" levels of PbO as measured by FPD at 200°C.

- Ambient particulate material was collected on Teflon filters for periods of 3 and 8 hr at 6 l/min; the filters were then used to collect sulfuric acid aerosol. For both levels of particulate loading the losses of the acid approached 90% as measured by FPD with volatilization at 200°C.

- Sulfuric acid aerosol was collected on Teflon filters; the filters were then used to sample ambient particulate material for 1 hr at 14 l/min. The average loss of sulfuric acid was 93% as measured by FPD at 150°C.

- Aerosols of ammonium sulfate salts were found to be a source of positive interference in the determination of sulfuric acid by FPD with volatilization at 200°C. Lowering the FPD volatilization temperature to 150°C reduced the contribution from the ammonium salts but also adversely affected the sensitivity of detection of sulfuric acid.

RESULTS OF EXPERIMENTS COLLECTING SULFURIC ACID AS A DERIVATIVE OF PERIMIDYLAMMONIUM BROMIDE (PDA-Br)

- Approximately 100 μg of ambient particulate material was collected on Teflon filters impregnated with the PDA-Br reagent. The filters were used to collect sulfuric acid aerosol and then analyzed by FPD with thermal decomposition at 450°C. The results suggested that sulfuric acid was completely recovered.

- Aerosols of the ammonium sulfate salts were collected on Teflon filters impregnated with PDA-Br and analyzed by FPD at 200 and 450°C. No response was found at 200°C, but the response found at 450°C indicated that PDA-Br was not selective for sulfuric acid since it appeared that the ammonium salts were also derivatized.

RESULTS OF EXPERIMENTS IN WHICH SULFURIC ACID WAS COLLECTED AFTER VOLATILIZATION AND PREFILTRATION

- Sulfuric acid aerosol was volatilized at a flow rate of 3 l/min in a heated sampling probe at 110°C. The vapors were then passed through a Teflon filter heated to 120°C. At least 90% of the resulting vapor passed the heated filter. The barium chloranilate (BCA) method was used for determination of sulfuric acid as sulfate.

- Ammonium sulfate aerosols were sampled under the same conditions with the heated sampling probe. BCA analysis showed that an average of 85% of the ammonium salts were retained by the heated (120°C) prefilter.

- Volatilized and prefiltered sulfuric acid was passed through filters impregnated with PDA-Br, sodium carbonate, or sodium hydroxide at 3 l/min. Very little of the sulfuric acid vapor was collected by the PDA-Br filters but an average of 60% was fixed by the sodium carbonate filters and 80% by the sodium hydroxide filters.

- An increase in the flow rate to 14 l/min was achieved with a new probe. The overall efficiency of the volatilization and prefiltration was lowered to 70% from a previous overall efficiency of 80% at 3 l/min. The efficiency was later increased to 80% by increasing the volatilization temperature to 130°C.

- The amount of sulfuric acid derivatized after volatilization and prefiltration at 14 l/min and 130°C was increased to greater than 90% using a disk-membrane Teflon filter impregnated with approximately 60 mg of sodium hydroxide. The filters were extracted ultrasonically and the sulfate concentration determined by ion chromatography.

- Ammonium sulfate aerosols were sampled with the heated sampling probe of 14 l/min and 130°C. Ion chromatographic analysis showed that greater than 99% of the ammonium sulfate salts were retained by the prefilter.

DEVELOPMENT OF A PROTOTYPE SAMPLER FOR SULFURIC ACID AEROSOL

- The sampling apparatus for sulfuric acid aerosol based on the volatilization, prefiltration, and derivatization methodology was incorporated into a prototype sampler.

- A gas diffusion denuder was used to remove more than 99% of the sulfur oxide gases from the sampled airstream since these gases could be converted to sulfate by the alkali-impregnated filter.

- A second denuder was used to remove like amounts of ammonia from the sampled airstream to prevent the reaction of ammonia with the volatilized sulfuric acid to form sulfate salts which could be removed by the prefilter.

- A dehumidifier was necessary to prevent the build-up of water vapor in the two denuders.

- The overall efficiency of the prototype sampler collecting laboratory-generated sulfuric acid aerosol at low concentrations was 83%. The minimum detectable level of the prototype sampler was approximately 0.5 $\mu g/m^3$.

RESULTS OF FIELD EVALUATION OF THE PROTOTYPE SAMPLER

- The prototype sampler was operated at two local roadside sites in the Birmingham, Alabama, area. Two control samples were collected with each sample to determine the amount of total sulfate and sulfates less than 2 μm in diameter present at each sampling site.

- Approximately 20% of the nonsized sulfate collected beside a city street with an average traffic flow of approximately 600 cars per hour was found to be sulfuric acid aerosol.
- Approximately 30% of the nonsized sulfate collected beside an interstate highway with an average traffic flow of 8,000 to 10,000 cars per hour was found to be sulfuric acid aerosol.

SECTION 4

EXPERIMENTAL APPARATUS AND PROCEDURES FOR COLLECTION OF SULFURIC ACID AEROSOL BY CONVENTIONAL METHODS

SULFURIC ACID AEROSOL GENERATOR

Operating Parameters

A modified version of the generator described by Thomas et al.* was used for laboratory studies with sulfuric acid aerosol. The use of this system, which was constructed and used in earlier work at Southern Research Institute (under EPA Contract No. 68-02-2234), was continued because it was shown to have certain attributes that were considered to be desirable for the purposes of this project. In particular, no other generator system could be expected to produce predominantly submicron particles, while simultaneously permitting flexibility for the addition of potential gaseous and particulate interferents directly to the aerosol. It also allowed easy adjustment of concentrations, particle size, flow rates, and other parameters.

The generator is illustrated in Figure 1. Its principal component was a Beckman No. 4020 atomizer-burner situated at the base of a 1.22-m by 99-mm i.d. Pyrex chimney. The fuel gas was hydrogen and the oxidizer was a mixture of oxygen and argon. A dilute solution of sulfuric acid was aspirated into the flame from a beaker placed underneath the burner. The ends of two 13-mm i.d. glass probes were located close together about 10 cm below the top of the chimney. One of these probes had a side arm closed with a silicone septum through which gases could be added at known flow rates. The probes were connected to stainless steel holders for 47-mm filters or impinger-bubblers which were followed by 6-l/min critical orifices and a carbon-vane vacuum pump. One side of this dual sampling system was always used as the reference for determination of the concentration of the sulfuric acid aerosol, while the other side was used for the introduction of interferent gases or for holding an impregnated

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*Thomas, R.L., V. Dharmarajan, and P.W. West. Convenient Method for Generation of Sulfuric Acid Aerosol, Environ. Sci. Technol., 8(10):930-935, 1974

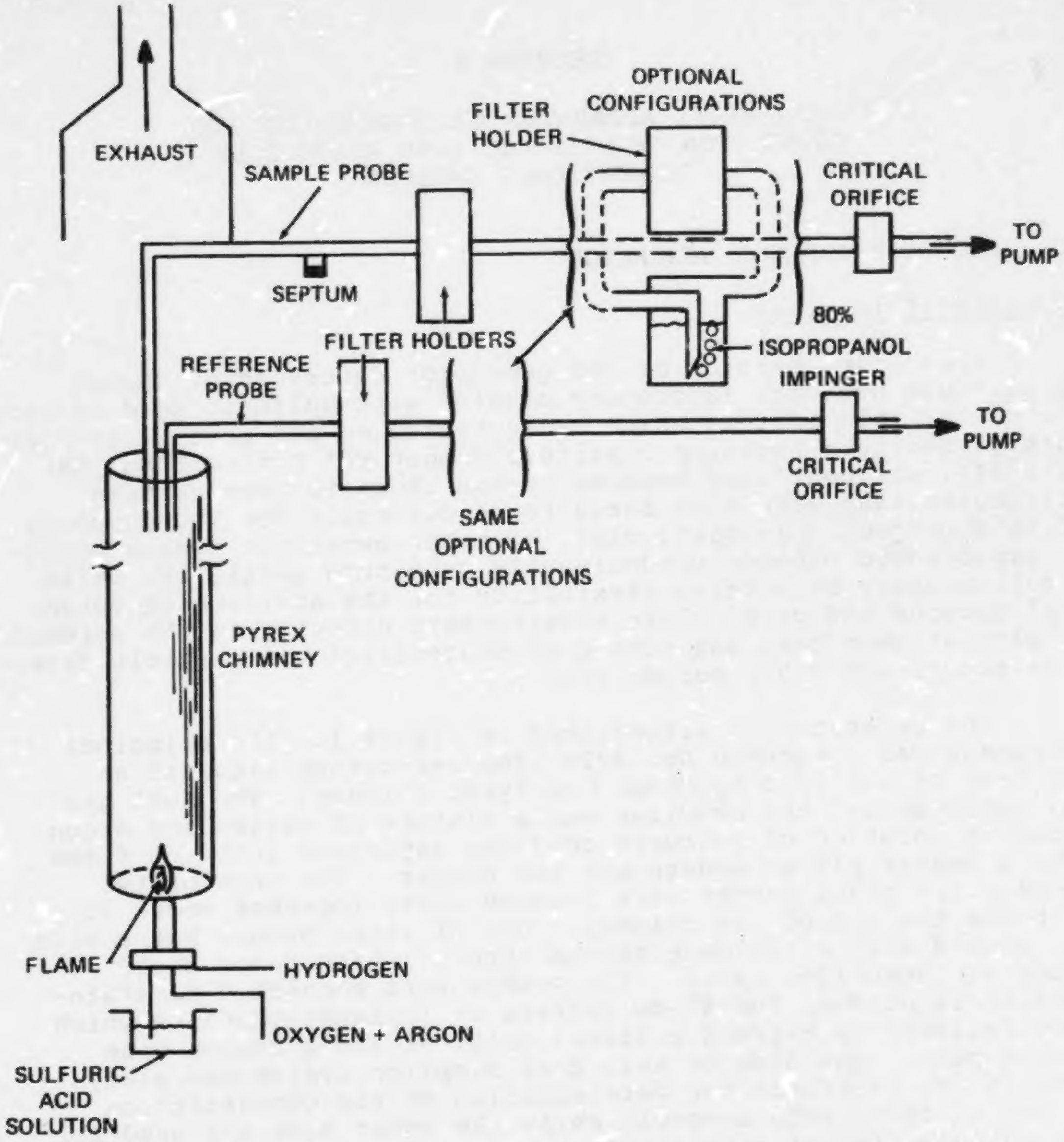
OPTIONAL
CONFIGURATIONS
FILTER
HOLDER
EXHAUST
SAMPLE PROBE
CRITICAL
ORIFICE
TO
PUMP
SEPTUM
80%
FILTER HOLDERS
ISOPROPANOL
IMPINGER
REFERENCE
PROBE
TO
PUMP
CRITICAL
ORIFICE
SAME
OPTIONAL
CONFIGURATIONS
PYREX
CHIMNEY
FLAME
HYDROGEN
OXYGEN + ARGON
SULFURIC
ACID
SOLUTION

Figure 1. Schematic of sulfuric acid aerosol generator (not to scale).

filter or a filter containing predeposited particulate material. The excess aerosol from the top of the chimney was exhausted through a hood.

The basic operating parameters for the aerosol generator and their typical values are shown in Table 1. All of these parameters were varied experimentally in order to find the optimum set of conditions. Data indicating typical amounts of sulfuric acid aerosol collected during operation of the laboratory generator are given in Table 2.

Aerosol samples usually containing 20 to 60 μg of sulfuric acid were collected on 47-mm Mitex filter disks in the experimental work. Smaller disks (ca. 6.3 mm) were punched from the experimental filters for analysis in the useful range of the flame photometric detector (FPD). Each small disk represented about 3.3% of the effective area of the sample that is collected on a 47-mm disk. Each FPD analysis reported for the filters was calculated to give the total on the 47-mm filter. Triplicate samples were taken from each filter by punching three 6.3-mm disks equidistantly from the center. The "A" and "B" samples in Table 2 were obtained simultaneously with a parallel sampling arrangement. These data showed that while a 10-min sample collected approximately one-half of the sulfuric acid that was obtained with the 20-min sample, the 5-min sample collected somewhat less than one-fourth. These results suggested that a small, relatively constant loss of sulfuric acid probably occurred in the handling of samples prior to analysis. This loss was probably less than 10% of the 20-min samples but may have been as much as 50% of the 5-min samples. The nature of this loss of sulfuric acid is uncertain but may be due to reaction of the acid with the ambient ammonia present in the laboratory. Levels of ambient ammonia were previously determined to be typically on the order of 4 mg/m^3 (see p. 38 of this report).

Background Contamination

Nitrogen Dioxide Concentration--

Measurements of the concentration of nitrogen dioxide in the effluent of the sulfuric acid aerosol generator were made previously under different operating parameters for the generator. At that time, argon was not used for dilution of the hydrogen-oxygen flame and effluent temperatures were substantially higher (ca. 100°C) Levels of nitrogen dioxide were found to be as high as 6 mg/m^3 under these conditions and attempts were subsequently made to minimize this concentration. Addition of argon to the flame in conjunction with lower pressures of hydrogen and oxygen resulted in lower effluent temperatures of approximately 30 to 35°C and a lower nitrogen dioxide concentration of 0.11 mg/m^3.

TABLE 1. AEROSOL GENERATOR STANDARD OPERATING PARAMETERS

- Feed solution—4 x 10^{-3} N H_2SO_4
- Positive burner pressures—H_2, 1.8 kPa (13.5 mmHg)
  O_2, 18 kPa (135 mmHg)
  Ar, 120 kPa (900 mmHg)
- Aspiration rate—*ca*. 2 ml/min
- Aerosol concentration—*ca*. 500 µg/m^3
- Sampling rate—6 l/min
- Sampling time—5 to 20 min
- Typical sample size—30 to 60 µg H_2SO_4
- Probe temperature—30 to 40°C

TABLE 2. SULFURIC ACID COLLECTED FROM THE GENERATOR AS A FUNCTION OF SAMPLING TIME

Sampling time, min	H_2SO_4 found on parallel 47-mm filters, µg*	
	A	B
20	54	59
20	60	52
10	32	26
5	8	8

* Each value is the average of triplicate analyses with the FPD technique using the square roots of the measured peak heights on a relative scale to determine the amount of H_2SO_4. These data exhibited a relative standard deviation of typically less than ca. 10 to 20%. The significance of the "A" and "B" samples is explained on the next page.

The conditions for the operation of the aerosol generator during these measurements were the same as those given in Table 1. The nigrogen dioxide concentration was determined by a method based on the Griess-Saltzman reaction as described in Intersociety Committee Method 42601-01-68T.

The ambient level of nitrogen dioxide was measured simultaneously with that of the generator and was determined to be about 0.05 mg/m^3 or approximately one-half of the level present in the effluent of the generator. Therefore, the nitrogen dioxide concentration in the generator effluent was judged to be low enough under current operating parameters for our work.

Sulfur Dioxide Content--

Previous attempts to use the West-Gaeke method (Intersociety Committee Method 42401-01-69T) to determine the concentration of sulfur dioxide in the effluent of the aerosol generator were not successful.* However, because different operating parameters were later used for the aerosol generator, the measurements were repeated. The results of these experiments are shown in Table 3. Essentially, these results were identical to those obtained earlier; that is, no sulfur dioxide could be detected. Moreover, as before, spikes of sulfur dioxide added to the tetrachloromercurate absorbing solution either before or after sampling the generator effluent could not be recovered. Thus, it appeared that the tetrachloromercurate-sulfur dioxide complex was decomposed by some component of the effluent produced by the aerosol generator. Due to the fact that sulfuric acid was eliminated as the cause of the interference (second entry in Table 3), no further explanation for this phenomenon can be offered. However, based on these results and those of previous work, it can be concluded that sulfur dioxide is not stable in the presence of the gaseous combustion products of the flame and is probably oxidized rapidly to sulfate.

Particle Distribution

Estimates of the particle-size and particle-mass distributions of the aerosol produced by the sulfuric acid generator were made with a Model 3030 Thermo-Systems Electrical Aerosol Size Analyzer (EAA) and a modified Climet Particle Analyzer. These measurements were made with the generator operating under the conditions given in Table 1. The results of these measurements are presented graphically in Figures 2 through 4.

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*Barrett, W.J., H.C. Miller, J.E. Smith, Jr., and C.H. Gwin. Southern Research Institute. Development of a Portable Device to Collect Sulfuric Acid Aerosol. EPA-600/2-77-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977. pp 15-16.

TABLE 3. DETERMINATION OF SO_2 CONCENTRATION IN THE H_2SO_4 AEROSOL GENERATOR WITH THE WEST-GAEKE METHOD

	SO_2 found, μg
Standard, 20 μg of SO_2 (as Na_2SO_3)	20
Standard, 20 μg of SO_2 (as Na_2SO_3) and 59 μg of H_2SO_4 (standard aqueous solution)	23
Sample collected from H_2SO_4 aerosol generator*	0.4
Sample collected from H_2SO_4 aerosol generator with spike of 20 μg of SO_2 (as Na_2SO_3) added to bubbler solution after sampling*	0.4
Sample collected from H_2SO_4 aerosol generator with spike of 20 μg of SO_2 (as Na_2SO_3) added to bubbler solution before sampling*	0.8

* Samples were collected for 20 min at a flow rate of 6 l/min.

Figure 2, which is a plot of the slope of the cumulative number distribution as a function of particle diameter, indicates that the majority of the aerosol particles had a diameter of less than 0.1 μm. On the other hand, it can be ascertained from Figures 3 and 4, which are plots of the cumulative volume distribution and the slope of the cumulative volume distribution, respectively, both as a function of particle diameter, that approximately 80% of the mass of aerosol particles was accounted for by those having a diameter between 0.2 and 1.5 μm.

It was found in an earlier evaluation of the particle distribution that more than 98% of both total mass and number of particles was associated with those smaller than 0.3 μm. These measurements were made during the time when operating conditions for the generator were such that the effluent temperature was in excess of 80°C. A comparison of the more recent results with those obtained earlier suggested that the overall particle distribution of the output of the aerosol generator was a sensitive function of the flame temperature. As a result, steps were taken to regulate accurately the fuel (hydrogen) pressure of the atomizer-burner in order to control the characteristics of the effluent aerosol.

Although the sulfuric acid generator does not produce an "ultrafine" aerosol with the current operating parameters, it appears that with appropriate adjustment of fuel, oxidant, and

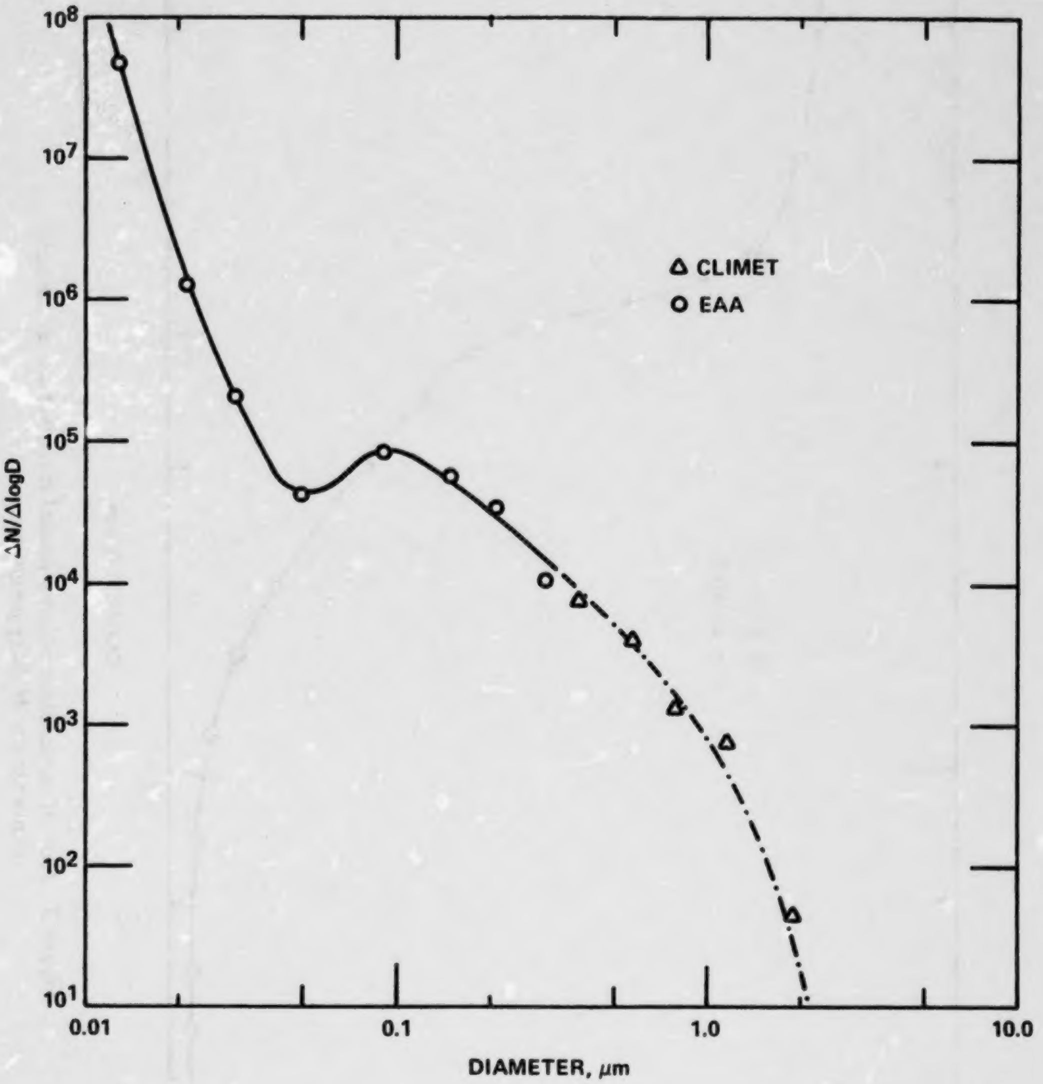

Figure 2. Plot of slope of cumulative number distribution vs. particle diameter for H_2SO_4 generator.

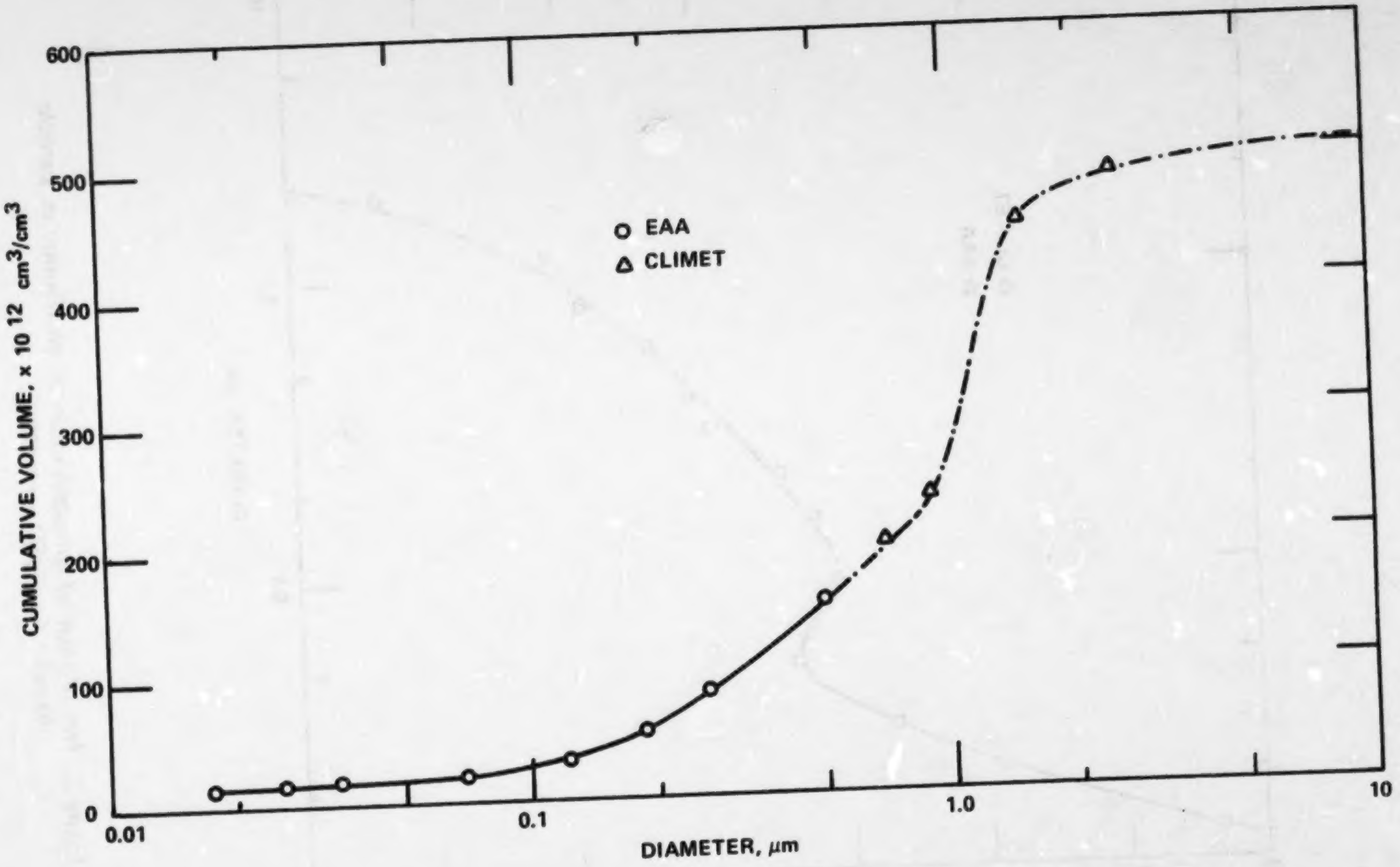

Figure 3. *Plot of cumulative volume (mass) distribution vs. particle diameter for H_2SO_4 generator.*

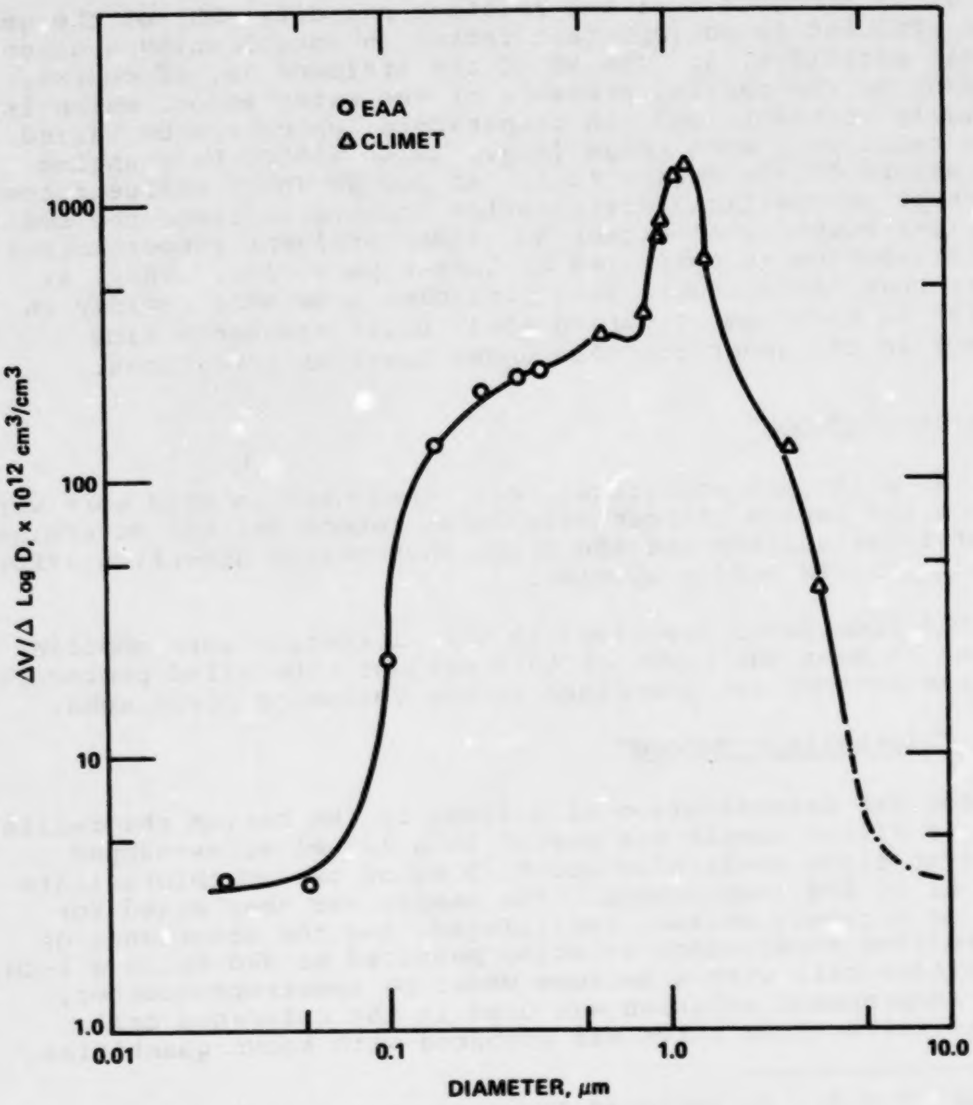

Figure 4. Plot of slope of cumulative volume distribution vs. particle diameter for H_2SO_4 generator.

diluent gas pressures the output can be varied to produce an aerosol of a given distribution over a reasonably broad range of particle sizes. However, the generator should be operated within constraints necessary to avoid high concentrations of potential interferents, such as nitrogen dioxide, and excessive effluent temperatures, which can promote vaporization of the sulfuric acid aerosol.

It is probable that the relative humidity (RH) of the generator effluent is an important factor in establishing a given particle distribution. The RH of the effluent is, of course, dependent on the partial pressure of the water vapor, which is relatively constant, and the temperature, which can be varied over a relatively wide range (e.g., 30 to 150°C) by changing the pressure of the burner fuel. At low RH (high effluent temperatures) the particle distribution appears to favor the smaller particles; however, at higher RH (lower effluent temperatures) the distribution is dominated by larger particles. Thus, it appears that the sulfuric acid particles grow more rapidly in the high RH environment during their brief residence time (<1 sec) in the generator than under lower RH conditions.

ANALYTICAL METHODS

The principal analytical techniques used in this work were based on the barium chloranilate (BCA) method for the determination of total sulfate and the flame photometric detection (FPD) of a volatilized sulfur species.

The procedures described in the literature were modified somewhat to meet the needs of this project. Detailed protocols for these methods are described in the following paragraphs.

Barium Chloranilate Method*

For the determination of sulfate by the barium chloranilate method, a filter sample was placed in a 125-ml screw-capped Erlenmeyer flask containing about 25 mg of barium chloranilate and 10 ml of 80% isopropanol. The sample was then mixed for 30 min on a rotary shaker, centrifuged, and the absorbance of the resulting supernatant solution measured at 310 nm in a 1-cm fused-silica cell with a Beckman Model DU spectrophotometer. An 80% isopropanol solution was used in the reference cell. A linear calibration curve was prepared with known quantities of standard sulfuric acid solutions that were treated in the same manner as experimental samples. The useful range of the method was 10 to 50 μg of sulfuric acid per filter without dilution of the sample.

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*Schafer, H.N.S. An Improved Spectrophotometric Method for the Determination of Sulfate with Barium Chloranilate as Applied to Coal Ash and Related Materials. Anal. Chem., 39(14:1719-1726, 1967.

Flame Photometric Detection of Volatilized Sulfuric Acid

Much of the work under the previous EPA contract (No. 68-02-2234) was intended to study the effect of selected interferent materials on the stability of sulfuric acid collected on filter media. Early in that study, analyses for sulfuric acid were conducted by selective extraction of the acid with benzaldehyde followed by a barium-Thorin microtitration of sulfate. However, in the later stages of the investigation, an FPD apparatus was constructed and successfully used to measure sulfuric acid. With this methodology the sulfuric acid was thermally volatilized from the filter medium and quantitated with the FPD. Analyses were performed more rapidly with this technique and the limit of detection was significantly lower than that of the "wet" methods employed earlier. One disadvantage of the FPD apparatus, however, was that the results obtained with it often possessed poor reproducibility.

Apparatus--

Early in the current contract (No. 68-02-2468) efforts were directed toward optimization of the FPD technique as it is applied to our program. First, in order to simplify the laboratory apparatus, the Model FPD 100AT flame photometric detector was removed from the Meloy Laboratories Model SA 160-2 Sulfur Gas Analyzer. This move facilitated the use of much shorter Teflon transfer lines from the volatilization chamber to the heated detector block. High voltage for the photomultiplier tube (PMT) of the FPD was provided by a Kepco Model ABC1500-M power supply, and the PMT current was measured with a Keithley Model 414A Picoammeter and an appropriate strip-chart recorder.

The sample chamber for thermal volatilization was also modified to improve reproducibility and to simplify the necessary manipulations during analysis. The glass chamber that was used previously was replaced with a Teflon-lined glass tube with significantly smaller surface area and "dead volume". A shorter Teflon transfer line was also made possible by replacing the aluminum heater block with a small tube furnace for maintaining the temperature of the sample chamber. The sample purging system was also modified to provide better control of the airflow necessary to sweep the sulfuric acid vapors from the sample chamber to the FPD. A schematic diagram of the FPD apparatus is shown in Figure 5.

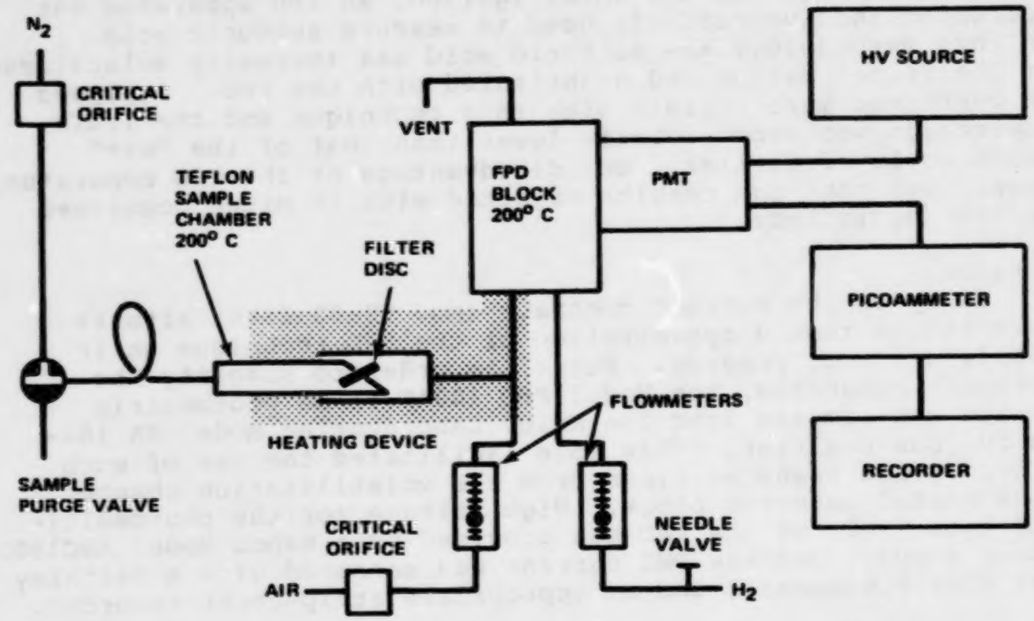
N_2
CRITICAL ORIFICE
TEFLON SAMPLE CHAMBER 200° C
FILTER DISC
VENT
FPD BLOCK 200° C
PMT
HV SOURCE
PICOAMMETER
RECORDER
FLOWMETERS
HEATING DEVICE
SAMPLE PURGE VALVE
CRITICAL ORIFICE
NEEDLE VALVE
AIR
H_2

Figure 5. Flame photometric detector apparatus for H_2SO_4 analysis.

Calibration with Known Amounts of Sulfuric Acid--
Several experiments were conducted to determine the practical working range for the quantitation of sulfuric acid with the FPD apparatus. Data for a calibration curve were obtained by measuring the peak height of the detector response as a function of the amount of sulfuric acid added to Mitex filters from standard solutions in isopropyl alcohol. In theory, the response of the FPD to a volatile sulfur species is proportional to the square of the sulfur mass concentration in the hydrogen-rich flame. As a test of this relationship and for purposes of calibration, the logarithms of the peak heights were plotted versus the logarithms of the corresponding amounts of sulfuric acid present in the standard samples. The theoretical slope of this plot should be 2, and a value of 2.09 was found experimentally. The linearity of this log-log calibration covered a useful range of approximately 0.1 to 2 µg of sulfuric acid per sample. Also, a relative standard deviation of 5.6% was obtained for 16 replicate analyses that were performed over a period of 2 weeks on standard samples at the 2-µg level. These results demonstrated that adequate sensitivity and reproducibility could be obtained with the FPD device.

For practical purposes, calibration curves were constructed from plots of the square root of detector response (peak height) versus micrograms of sulfuric acid. The advantage of this plot was that the calibration was linear in the amount of sulfuric acid. Typical calibration data are given in Table 4. These data are also shown graphically in Figure 6.

For purposes of calibration in early experiments the square root of the peak height of the FPD response provided a satisfactory linear correlation with the amount of sulfuric acid. However, a more rigorous treatment was later performed by linearization and integration of the sulfur-FPD peaks. The linearizer incorporated into the FPD apparatus electronically obtained the square root of the FPD signal and manual planimetry provided integration of the linearized peaks.

The method of calibration for the FPD varied during different phases of the project. The method used for calibration will be noted in the tables that give data from FPD determinations.

Calibration of the improved FPD apparatus with known amounts of sulfuric acid on Mitex filters produced the curves shown in Figures 7 and 8. The volatilization temperature used to obtain the data in Figure 7 was 200°C. The linear range of the calibration was found to be 2 to 20 µg of sulfuric acid per 47-mm filter disk (an accurately cut portion of the 47-mm filter was used for the analysis). The volatilization temperature for the data in Figure 8 was 150°C, and the linear range at this temperature

TABLE 4. DATA FOR THE CALIBRATION OF THE FPD APPARATUS

H_2SO_4 added,* µg	Square root of FPD response,† arbitrary units
2.05	17.0
	17.6
	17.9
1.23	10.4
	10.8
	10.2
0.82	7.1
	7.0
	6.9
0.33	2.0
	2.2
	2.3

* Standard solutions of sulfuric acid in isopropyl alcohol were applied to Mitex filters (6.3-mm disks) with microburet.

† These data are the square roots of the measured peak heights on a relative scale.

was 4 to 15 µg of sulfuric acid per 47-mm filter. The slight reduction in sensitivity was probably due to less efficient volatilization of the sulfuric acid from the Mitex filter and some adsorption on surfaces at the lower temperature. Poor reproducibility was also observed in the data for the calibration curve at 150 °C for amounts less than 1 µg. The reproducibility at lower levels was later improved with further instrument modifications (see p. 40 of this report).

FILTER MATERIALS

Mitex and Fluoropore are two types of Teflon (PTFE) filters that have been used for the collection of sulfuric acid aerosol. During previous contract work several measurements demonstrated that Mitex filters with a 5-µm pore size rating were 99% efficient in the collection of sulfuric acid aerosols with particle sizes in the range of 0.3 to 0.005 µm. However, because Fluoropore filters are frequently used by other workers for the collection of sulfuric acid aerosol, a comparison was made by sampling the laboratory generator simultaneously with Mitex and Fluoropore filters in parallel.

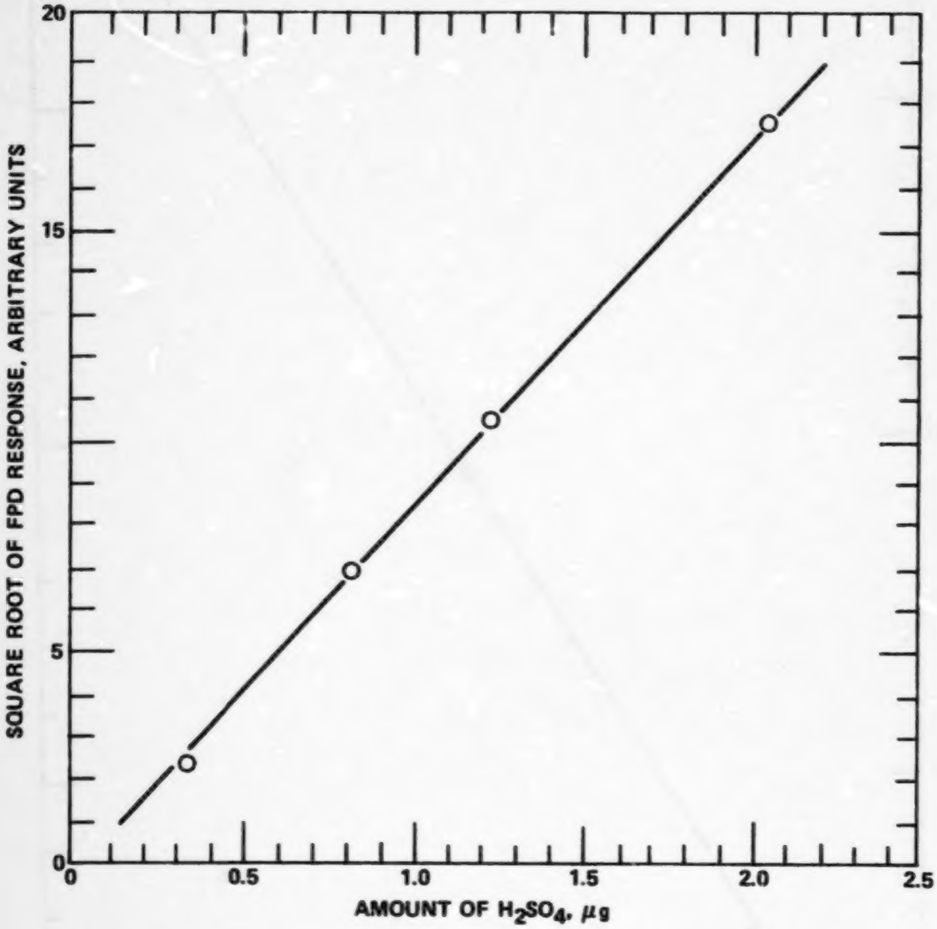

Figure 6. FPD calibration for H_2SO_4 deposited on filters and volatilized at 200°C.

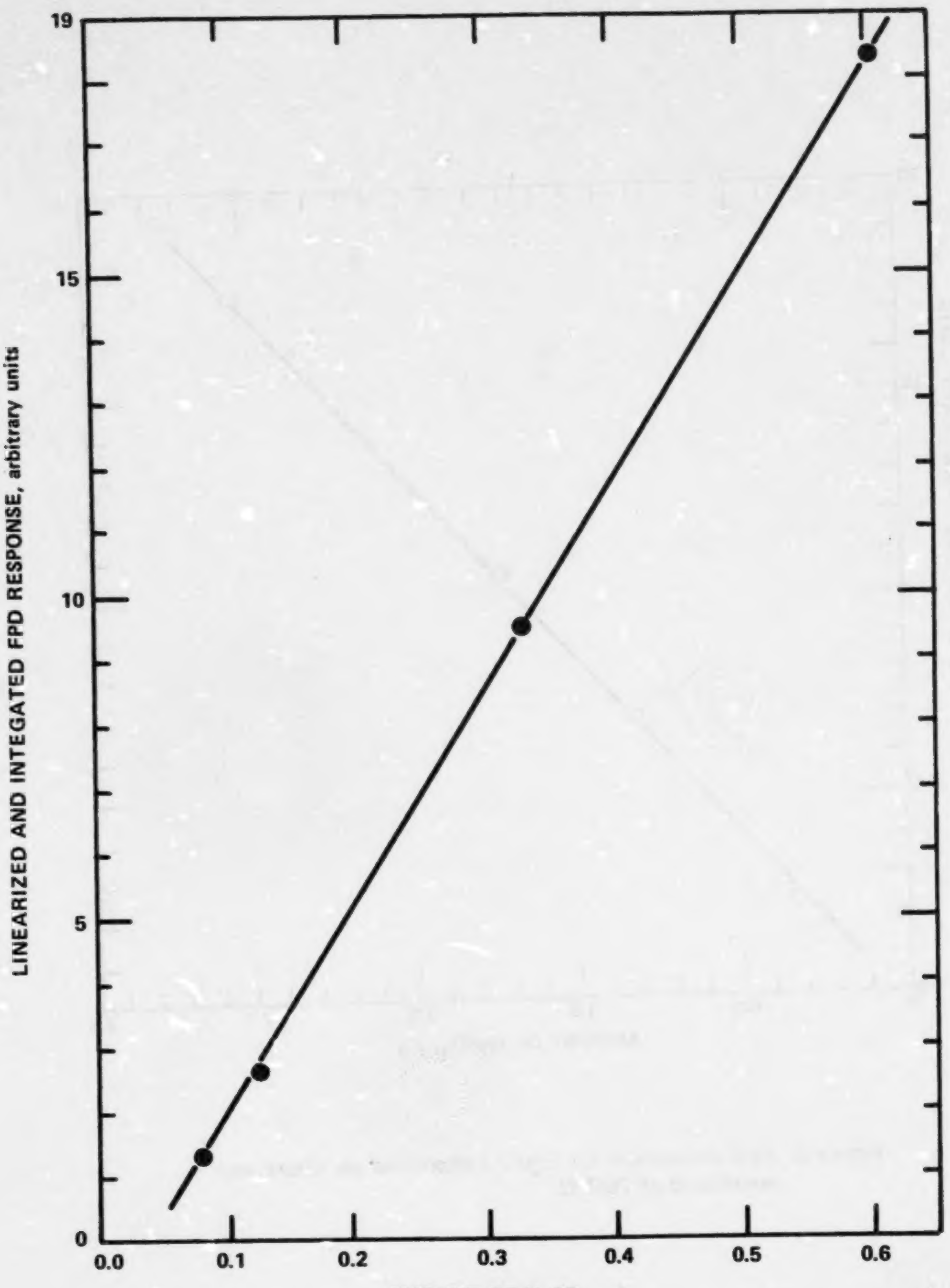

Figure 7. Calibration of modified FPD for H_2SO_4 deposited on filters and volatilized for analysis at 200°C.

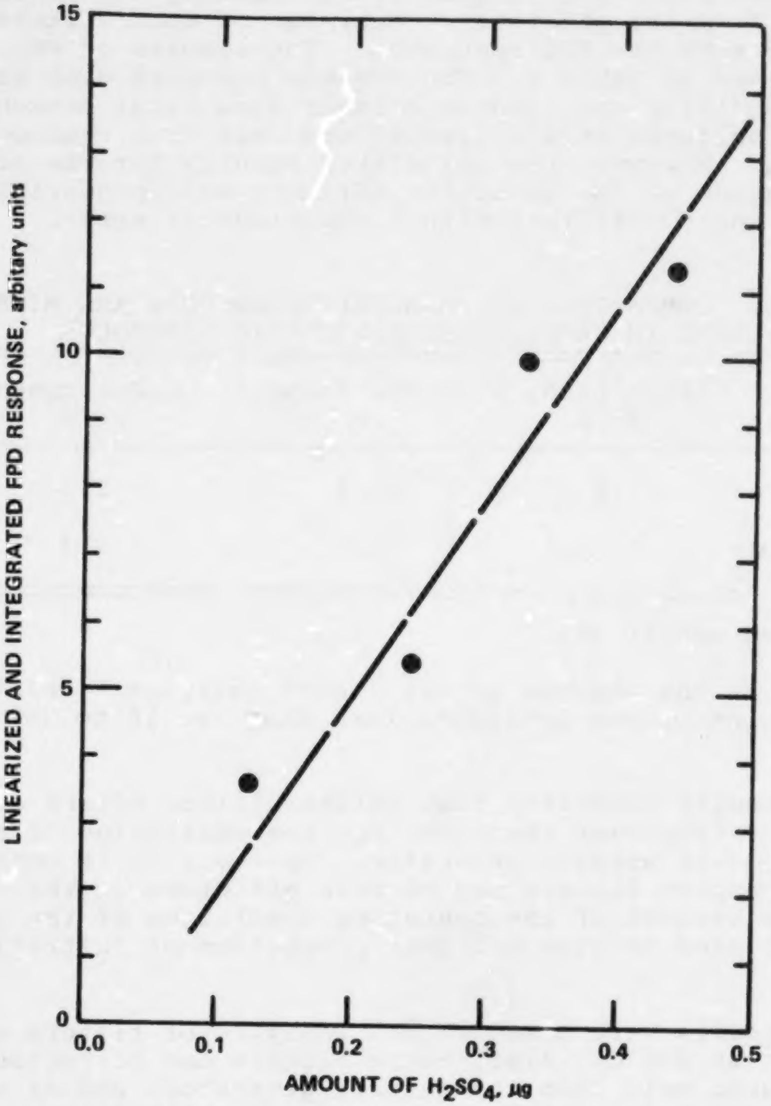

Figure 8. Calibration of modified FPD for H_2SO_4 deposited on filters and volatilized for analysis at 150°C.

Filter Evaluation with FPD Determinations

Mitex filters with a 5-μm pore size rating and Fluoropore filters (1-μm pore size) that are manufactured without the polyethylene backing were used simultaneously to collect sulfuric acid from the generator. Analyses of both filters were conducted with the FPD apparatus. The results of the comparison are given in Table 5. The greater pressure drop across the Fluoropore filter resulted in a lower flow rate; consequently, the amount of sulfuric acid collected was less than Fluoropore than for Mitex. However, the calculated results for the sulfuric acid concentration in the generator effluent were essentially identical for the two filters within experimental error.

Table 5. COMPARISON OF PARALLEL FLUOROPORE AND MITEX FILTERS IN SAMPLING SULFURIC ACID AEROSOL*

Filter material	Flow rate, l/min	H_2SO_4 found,† μg	H_2SO_4 concn, μg/m^3
Mitex	6.0	61.4	513
Fluoropore	5.2	55.4	533

* Sampling time was 20 min.

† Each result is the average of triplicate analyses. Relative standard deviation was typically less than ca. 10 to 20%.

These results suggested that neither filter offers any particular advantage over the other for the collection of sulfuric acid from the aerosol generator. However, it is conceivable that Fluoropore filters may be more efficient in the collection of the aerosol if the operating conditions of the generator were adjusted to give a higher proportion of "ultrafine" particles.

These results were based on FPD analysis of filters with volatilization at 200°C. Also, these filters had collected about 60 μg of sulfuric acid from the aerosol generator, and at that sulfuric acid level the results obtained with both filters were essentially the same. On the other hand, it had been observed earlier for smaller amounts of sulfuric acid aerosol (e.g., less than about 20 μg per 47-mm disk) that the recovery upon analysis was somewhat less than expected for Mitex filters. It appeared that a small, constant amount of sulfuric acid (ca. 5 μg) was not recovered from the Mitex filters. This amount was not significant at the 60-μg level and fell within the uncertainity of the FPD analyses, but at the 10- to 20-μg level the loss was substantial (25 to 50%).

In subsequent work this phenomenon was found to be more pronounced for Fluoropore filters than for Mitex. For example, collection of about 15 μg of sulfuric acid aerosol on Mitex filters (measured independently on a parallel filter by the BCA method for total sulfate) followed immediately by FPD analysis with volatilization at 200°C gave a result of only 8 μg or about 50% recovery. On the other hand, only about 6 μg of the acid was found by FPD analysis of a Fluoropore filter that had collected about 33 μg of aerosol (approximately 20% recovery).

These FPD results reported for the comparison of Mitex and Fluoropore filters were based on volatilization at 200°C; however, the recoveries were even lower at 150°C—the volatilization temperature necessary to minimize FPD interferences from the ammonium salts of sulfuric acid. For example, FPD determination of 36 μg of sulfuric acid aerosol collected on Fluoropore gave 12 μg at 200°C (about 35% recovery) and 3 μg at 150°C (about 10% recovery). With Mitex the results were somewhat better: for 19 μg of the aerosol, FPD determination at 200°C gave 14 μg (about 70% recovery) and at 150°C the result was 12 μg (about 65% recovery). Further, it should be noted that the determinations for each filter at both temperatures were referred to individual calibration curves. These curves were prepared from FPD responses, at the corresponding temperatures, to known spikes of sulfuric acid added to the appropriate filters from a solution in isopropanol.

Filter Evaluation with BCA Determinations

It was interesting also that the same phenomenon as described for FPD occurred with the BCA determinations of sulfate when the filters were not agitated ultrasonically during extraction into 80% isopropanol. That is, at the 70-μg level the recoveries were about 90% without ultrasonic extraction for both Mitex and Fluoropore filters spiked with known amounts of sulfuric acid, but at the 10-μg level the recoveries were only about 70% for Mitex and 50% for Fluoropore. However, with ultrasonic extraction the low level recoveries for both filters approached 100%. These results suggested that the sulfuric acid may have diffused into the interior pores of the filters where it was difficult to remove by extraction or thermal volatilization. The phenomenon appears to involve a constant amount of sulfuric acid and the situation seems to be worse with Fluoropore filters. The use of Teflon membrane filters may have reduced the severity of this effect, but these were not evaluated in this study due to the need for high sampling flow rates (ca. 14 l/min).

In conclusion, neither the Mitex nor Fluoropore filter appears to be entirely adequate for the thermal volatilization-FPD determination of sulfuric acid. However, the results tend to favor Mitex filters because of the substantially higher recoveries that were found relative to Fluoropore. In any event, these results further indicate problems in the conventional volatilization FPD analysis of sulfuric acid.

SECTION 5

INTERFERENCE STUDIES ASSOCIATED WITH THE COLLECTION OF SULFURIC ACID AEROSOL

COLLECTION OF SULFURIC ACID AEROSOL

The effect of selected interferent materials upon the stability of sulfuric acid collected on Teflon filter disks studied with quantitation of the acid with the FPD apparatus. The interferents were chosen from those representative of a roadside environment and those which have the potential to react with sulfuric acid. This study essentially concluded the interference studies that were begun under the previous EPA contract (No. 68-02-2234) concerning sulfuric acid aerosol.

Interference from Fe_2O_3

Experiments were conducted to measure the effect of Fe_2O_3 on the stability of sulfuric acid collected on a Mitex filter with analysis by the FPD method. A similar study was performed in previous work with analyses by the benzaldehyde extraction technique (specific for sulfuric acid) and insignificant losses of sulfuric acid were found. However, results of experiments with analyses by FPD indicated that substantial losses of acid occurred for the "high" levels of predeposited Fe_2O_3 as opposed to somewhat more moderate losses for the "low" level. These data are given in Table 6. The average recoveries of sulfuric acid sampled as aerosol following deposition of Fe_2O_3 were 18% for the "high" level and 79% for the "low" level. The Fe_2O_3 particulate was sampled from an aerosol produced by a DeVilbiss powder blower; no effort was made to characterize the size distribution of this aerosol. The two levels of Fe_2O_3 were obtained by sampling the aerosol ten times longer for the "high" level than for the "low" level.

Recoveries of spikes of sulfuric acid (in isopropanol solution) added to filters also depended upon the level of predeposited Fe_2O_3. Average recoveries of the spikes were 54% for the "high" level and 106% for the "low" level. Although the recoveries of spikes were adequate at the "low" level of Fe_2O_3, the greater losses of sulfuric acid for both spiked and aerosol samples at the "high" level could have resulted from further reaction of the residual acid with the additional Fe_2O_3 on the filter at the elevated temperature (ca. 200°C) of the FPD volatilization chamber. Accordingly, it is possible that the lower recoveries found with FPD analyses as opposed to those obtained earlier with the benzaldehyde extraction technique resulted from reaction of sulfuric acid with Fe_2O_3 during volatization in the FPD. However, the fact that the recoveries for the aerosol samples were lower than those of the spiked samples suggested that additional losses of acid might have occurred during aerosol sampling.

TABLE 6. EFFECT OF PREDEPOSITED Fe_2O_3 UPON SULFURIC ACID COLLECTED ON MITEX FILTERS

Fe_2O_3 added, mg	H_2SO_4 added,* µg	H_2SO_4 spike,† µg	H_2SO_4 found,§ µg	Recovery, %
High levels				
0.3	none	none	<0.1	-
0.6	none	63	34	54
0.3 (0.3)#	40 (47)	none	7.2 (44)	18 (96)
0.5	45	none	6.3	14
0.3	52	none	10.8	21
Low levels				
<0.1	none	none	<0.1	-
<0.1	none	63	67	106
<0.1	62	none	44	71
<0.1	64	none	54	84
<0.1	64	none	53	82

* The amount of sulfuric acid added was determined by analysis of a parallel filter exposed only to the sulfuric acid aerosol.

† The spike was added to the filter exposed to Fe_2O_3 from a standard solution of sulfuric acid in isopropyl alcohol.

§ Each result is the average of triplicate FPD determinations calculated from the square roots of the peak heights. Relative standard deviation was typically less than ca. 10 to 20%.

The numbers in parentheses are the results of similar experiments in which the analyses for sulfuric acid were conducted with the benzaldehyde extraction technique.

Interference from PbO

The evaluation of PbO as a cause of interference during the collection of sulfuric acid aerosol was conducted in the same manner as described earlier for Fe_2O_3. The results of these experiments are given in Table 7. Although there was a relatively large variability in replicate values for recovery of acid in the presence of PbO at the "high" level, it was evident that substantial losses of acid occurred. The same trend was observed with PbO as with Fe_2O_3 in that the losses of acid at the "low" level of interferent were significantly less than at the "high" level. These results cannot be compared with previous data because PbO was not included in interference studies conducted with the benzaldehyde extraction technique.

TABLE 7. EFFECT OF PREDEPOSITED PbO UPON SULFURIC ACID COLLECTED ON MITEX FILTERS

PbO added, mg	H_2SO_4 added, μg*	H_2SO_4 found, μg†	Recovery, %
High levels			
0.5	none	0.1	-
0.5	59	3.9	6
0.7	62	20	32
0.7	60	12	20
Low levels			
0.1	none	0.1	-
0.1	60	40	67
0.1	58	38	66
0.1	57	37	65

* The amount of sulfuric acid added was determined by analysis of a parallel filter exposed only to the sulfuric acid aerosol.

† Each result is the average of triplicate FPD determinations calculated from the square roots of the peak heights. Relative standard deviation was typically less than ca. 10 to 20%.

Interference from Ambient Particulate Material

The effect of ambient particulate material (APM) on the stability of sulfuric acid collected on a filter was studied in previous work with analyses by the benzaldehyde extraction technique. At that time, losses of sulfuric acid approaching 70% were found for collection of the acid aerosol on filters previously exposed to APM. Because the effect of ambient particulate is important and was studied with FPD analyses only semiquantitatively in our earlier work, this potential interferent was evaluated again with the improved, more nearly quantitative FPD technique.

The APM was collected on 47-mm Mitex filters beside a busy roadway in Birmingham. Because typical sampling times were several hundred min for collection of APM and only 15 min for collection of laboratory-generated sulfuric acid aerosol, the aerosol could not be collected simultaneously. Rather we chose to study the effects of collection of sulfuric acid "early" and "late" in the ambient sampling period.

The results of the FPD determinations of sulfuric acid added to the filters from the aerosol generator are given in Table 8. The recoveries of sulfuric acid were determined for two levels of APM—the "high" level representing an 8-h sampling period and the "low" level, a 3-h sample. These data demonstrated, again, the severe losses of sulfuric acid that can occur in the presence of ambient particulate on a filter disk. For both the "high" and "low" levels of particulate, the losses of the acid approached 90%, which was somewhat more than determined by the wet methods of analysis that were used earlier. The greater losses of sulfuric acid that were determined by FPD analyses could have resulted from further reaction of the residual acid with the particulate on the filter at the elevated temperature (ca. 200°C) of the FPD volatilization chamber. In any event, the addition of a spike of sulfuric acid in isopropyl alcohol to a filter exposed to APM also resulted in a low recovery of the acid (ca. 18%).

On the other hand, detectable FPD responses were routinely observed for filters containing only the APM. The response could possibly be due to a sulfur species other than sulfuric acid; however, the concentration of ambient sulfuric acid calculated from these data was approximately 1 to 2 $\mu g/m^3$. These data are also in approximate agreement with earlier results obtained with wet methods.

Experiments were also conducted in which the order of collection of APM and sulfuric acid was reversed. First, known amounts of sulfuric acid from the aerosol generator were deposited on Mitex filters, and then APM was collected, either in the laboratory or near a street with heavy traffic. The experimental conditions and the results of the FPD analyses are presented in Table 9. The recoveries of sulfuric acid were much greater than when APM was deposited first.

Essentially all of the sulfuric acid was recovered from the filters exposed at the roadside and about two-thirds was recovered from the filters exposed in the laboratory.

TABLE 8. EFFECT OF PREDEPOSITED AMBIENT PARTICULATE MATERIAL UPON SULFURIC ACID COLLECTED ON MITEX FILTERS

Ambient particulate added, mg	H_2SO_4 added,* µg	H_2SO_4 spike,† µg	H_2SO_4 found,§ µg	Recovery, %
High				
0.3 (0.3)#	none	none	5.3 (4)	-
0.3	none	63	11.1	18
0.1 (2.0)	68 (29)	none	7.1 (10)	10 (34)
0.2	54	none	5.2	10
0.3	65	none	7.6	12
Low				
<0.1	none	none	3.9	-
<0.1	60	none	6.4	11
<0.1	58	none	8.5	15
<0.1	57	none	5.4	10

* The amount of sulfuric acid added was determined by analysis of a parallel filter exposed only to the sulfuric acid aerosol.

† The spike was added to the filter exposed to ambient particulate material from a standard solution of sulfuric acid in isopropyl alcohol.

§ Each result is the average of triplicate FPD determinations calculated from the square roots of the peak heights. Relative standard deviation was typically less than ca. 10 to 20%.

The numbers in parentheses are the results of similar experiments in which the analyses for sulfuric acid were conducted with the benzaldehyde extraction technique.

TABLE 9. EFFECT OF AMBIENT PARTICULATE MATERIAL ON FPD MEASUREMENT OF SULFURIC ACID PREDEPOSITED ON MITEX FILTERS

Sampling time,* min	H_2SO_4 added,† μg	H_2SO_4 found,§ μg	Recovery,# %
Roadside atmosphere			
5	45	45	100
10	45	44	98
20	46	46	100
40	41	40	98
60	41	34	83
180	0	4	-
Laboratory atmosphere			
40	55	36	65
180	58	39	67
300	57	39	68
360	57	42	74
300	0	6	-

---

* Sampling rate was 6 l/min at a level of APM of about 100 μg/m^3.

† The amount of sulfuric acid added was determined by analysis of a parallel filter exposed only to the sulfuric acid aerosol.

§ Each result of the average of triplicate FPD determinations calculated from the square roots of the peak heights. Relative standard deviation was typically less than ca. 10 to 20%. The temperature of the volatilization chamber was 200°C.

# Explanations of the trends of these recoveries and those reported in Table 8 are set forth in the following discussion.

The two most important factors likely to influence the results of these experiments are neutralization of the acid by ambient ammonia and reaction of the collected sulfuric acid with alkaline particulate materials on the filter. It was expected that when the sulfuric acid was deposited first, neutralization by ambient ammonia during subsequent collection of the APM would cause loss of the acid. Based on an estimate of the amount of ammonia sampled simultaneously with the APM, partial losses of sulfuric acid were expected for sampling times under 80 min and total losses for sampling times substantially over 80 min. The results, however, were not consistent with this expectation. If reaction of the predeposited acid with ammonia did occur, then it appeared that positive interference was caused by decomposition of the resulting ammonium salts at 200°C. Another conceivable explanation of the high recoveries is that neutralization by ammonia did not occur, at least not completely and that the predeposited sulfuric acid diffused into the interior pores of the filter where it could not react with alkaline particulate material.

INTERFERENCE FROM AMMONIUM SALTS OF SULFURIC ACID

Several uncertainties resulted from the experiments described above in which sulfuric acid deposited on Mitex filters was exposed to ambient particulate material (APM). The principal uncertainties involved recoveries of sulfuric acid that were higher than expected based on the measured concentration of ambient ammonia that was sampled simultaneously with the ambient particulate material. These results suggested the possibility of positive interference from ammonium salts in the FPD analysis at 200°C. Subsequently, a study of the interferences from ammonium sulfate and ammonium bisulfate was performed by applying either aqueous or alcoholic solutions of the salts to Mitex filters followed by FPD analysis. The results of these experiments are given in Table 10. Although these data are not comprehensive and are of limited significance, it appeared that the FPD response was dependent on the temperature of the volatilization chamber. Both ammonium salts gave positive responses at the 200°C volatilization temperature but no significant response was observed at 150°C with either. Because of these findings, the evaluation of APM as a possible interferent in the collection of sulfuric acid aerosol was repeated with attention to the temperature of volatilization in the FPD analysis.

INTERFERENCE FROM AMBIENT PARTICULATE MATERIAL—ANALYSIS CORRECTED FOR INTERFERENCE FROM AMMONIUM SALTS

The evaluation of APM as an interference in the collection of sulfuric acid aerosol was continued with experiments in which a cyclone was used in ambient sampling to eliminate particles greater than about 2 μm in diameter. A description of the cyclone is given in a report prepared by Southern Research Institute for the Environmental Protection Agency (EPA 650/2-74-102-a, August 1975). Our work in the past had not included size fractionation of APM collected for interference studies. However, by eliminating the larger particles the evaluation of interference due to APM becomes more realistic in relation to some of the state-of-the-art devices that have been developed for sampling analysis of ambient aerosols of sulfuric acid. Also, in these experiments the temperature of the volatilization chamber was adjusted to 150°C to reduce interference from ammonium salts.

TABLE 10. INTERFERENCE FROM AMMONIUM SALTS OF SULFURIC ACID IN FPD ANALYSIS

Ammonium salt added, μg	FPD response as H_2SO_4, μg*	
	200°C	150°C
NH_4HSO_4		
0.32†	0.12	0
0.32§	0.08	0
>100#	1.14	0
$(NH_4)_2SO_4$		
0.32†	0.09	0
0.34§	0.09	0
>>100#	0.34	0.1

* The values are the averages of triplicate FPD determinations calculated from the square roots of the peak heights. Relative standard deviation was typically less than ca. 10 to 20%.

† A standard solution of the salt in 80% isopropyl alcohol was applied to Mitex filters.

§ A standard solution of the salt in water was applied to Mitex filters.

# A small crystal of the ammonium salt was placed on the filter.

Predeposition of Particulate Material

Table 11 gives the results of FPD measurement of sulfuric acid aerosol collected from the laboratory generator on Mitex filters after sampling APM. Because of the complex nature of the interaction of APM and sulfuric acid aerosol during sampling, these data collectively possessed poor reproducibility. However, the precision of the individual measurements on a given sample was satisfactory (typically less than 10 to 20% RSD).

From the data obtained with the cyclone it appeared that the extent of reaction of sulfuric acid with APM was a function of the concentration of total ambient particulates. In these experiments, higher recoveries of sulfuric acid resulted when ambient sampling was done at the lower concentration of APM. Sampling of APM without the cyclone did not appear to reduce the recovery of the sulfuric acid solution compared with that observed for experiments with the cyclone. In any event, these results indicated that trends observed in previous studies of interference from APM with the FPD determination and the benzaldehyde extraction technique are valid.

TABLE 11. RESULTS OF FPD MEASUREMENT OF SULFURIC ACID COLLECTED ON MITEX FILTERS FOLLOWING COLLECTION ON AMBIENT PARTICULATE MATERIAL

Ambient particulate added, µg*	H_2SO_4 aerosol added, µg†	H_2SO_4 spike, µg§	H_2SO_4 found, µg#	Recovery, %
Without cyclone				
~90 (109 $\mu g/m^3$)**	none	none	0.6	-
~90	none	13.7	4.0	29
~90	none	13.7	4.0	29
~90	10.1	none	2.0	20
~90	7.0	none	1.6	23
~90	9.2	none	2.2	24
With cyclone††				
<50 (68 $\mu g/m^3$)	none	none	0	-
<50	none	13.7	11.4	83
<50	none	13.7	8.3	61
<50	15.4	none	5.9	38
<50	11.2	none	4.8	43
<50	12.2	none	6.4	52
<90 (109 $\mu g/m^3$)	none	none	0.5	-
<90	none	13.7	7.1	52
<90	none	13.7	5.6	41
<90	8.3	none	1.3	16
<90	11.5	none	1.9	9
<90	9.4	none	1.6	17

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* The sampling rate was 14.1 l/min for 1 hr.

† Analysis of a parallel filter exposed only to the sulfuric acid aerosol was used to determine the amount of sulfuric acid added.

§ The spike was added from a standard solution of sulfuric acid in isopropyl alcohol.

# Each result is the average of triplicate FPD determinations calculated from the square roots of the peak heights. Relative standard deviation was typically less than ca. 10 to 20%. The temperature of the volatilization chamber was 150°C.

** The numbers in the parentheses are the total ambient particulate levels during sampling.

†† An uncertain fraction of the particulate material in the air sampled was removed by the cyclone.

Predeposition of Sulfuric Acid

Table 12 gives the results of FPD measurements of sulfuric acid when the acid aerosol was collected before sampling APM. Calculations based on a measured concentration of ambient ammonia of 3.6 mg/m^3 indicated that sufficient ammonia was present in the 0.83 m^3 of sampled air to neutralize all of the predeposited sulfuric acid. The results of the FPD analyses for this experiment agreed with this assumption due to the low recoveries of sulfuric acid found with the 150°C volatilization temperature. Thus, the higher recoveries reported earlier from identical experiments, except for volatilization interference by ammonium salts that were formed on the filter during the sampling of APM. Furthermore, the use of the cyclone for size discrimination of the APM would not be expected to alter these results.

CONCLUSION

Although the severity of the interference from APM in the collection of sulfuric acid aerosol appeared to be dependent upon the level of ambient particulate, the interference was generally sufficient in any event to complicate the accurate measurement of the concentration of sulfuric acid aerosol by FPD. Of equal importance is the additional interference due to ambient ammonia that is sampled simultaneously with the sulfuric acid.

TABLE 12. RESULTS OF FPD MEASUREMENTS OF SULFURIC ACID COLLECTED ON MITEX FILTERS PRIOR TO COLLECTION OF AMBIENT PARTICULATE MATERIAL*

Ambient particulate added, μg†	H_2SO_4 aerosol added, μg§	H_2SO_4 spike, μg#	H_2SO_4 found, μg**	Recovery, %
35 (45 μg/m³)††	none	none	0	–
35	none	13.7	6.5	47
35	none	13.7	6.2	45
35	13.1	none	0.6	5
35	8.9	none	0.8	9
35	9.6	none	0.6	6
35	10.7	none	0.8	7

* Size discrimination of APM was not used for these experiments.

† The sampling rate was 14.1 l/min for 1 hr.

§ Analysis of a parallel filter exposed only to the sulfuric acid aerosol was used to determine the amount of sulfuric acid added.

# The spike was added from a standard solution of sulfuric acid in isopropyl alcohol.

** Each result is the average of triplicate FPD determinations calculated from the square roots of the peak heights. Relative standard deviation was typically less than ca. 10 to 20%. The temperature of the volatilization chamber was 150°C.

†† The number in parentheses is the total ambient particulate level during sampling.

SECTION 6

EXPERIMENTAL APPARATUS AND PROCEDURES FOR COLLECTION OF SULFURIC ACID AEROSOL BY DERIVATIZATION METHODS

In light of the results of the interference studies with the conventional collection methods, it became apparent that it would be necessary to collect the sulfuric acid aerosol as a stabilized derivative. The first derivatization technique investigated was based on the reaction of sulfuric acid aerosol with perimidylammonium bromide (PDA-Br). Later, experiments were performed to determine if sulfuric acid aerosol could be volatilized during sampling and solid interferents such as ammonium sulfates of lower volatility removed by filtration of the heated airstream prior to derivatization of the volatilized sulfuric acid.

ANALTYICAL METHODS

The principle analytical techniques used in developing the derivatization methods were based on the flame photometric detection (FPD) of a volatilized sulfur species, the barium chloranilate (BCA) method for the determination of total sulfate, and ion chromatography (IC) for the determination of total sulfate in the presence of ions which interfere with the BCA and FPD methods.

Modified Flame Photometric Detector Apparatus

Modifications to the FPD Apparatus--

Modifications were made to the FPD apparatus described in Section 4. The major change was the addition to the apparatus of the second volatilization chamber. Figure 9 depicts the apparatus in its final stage of development. The use of two separate chambers allowed the determination of sulfuric acid at volatilization temperatures from 150 to 200°C and the perimidylammonium sulfate (PDA-SO_4) derivative at its decomposition temperature of 450°C. Teflon tubing was used to replace all metal transfer lines from the volatilization chambers to the FPD block.

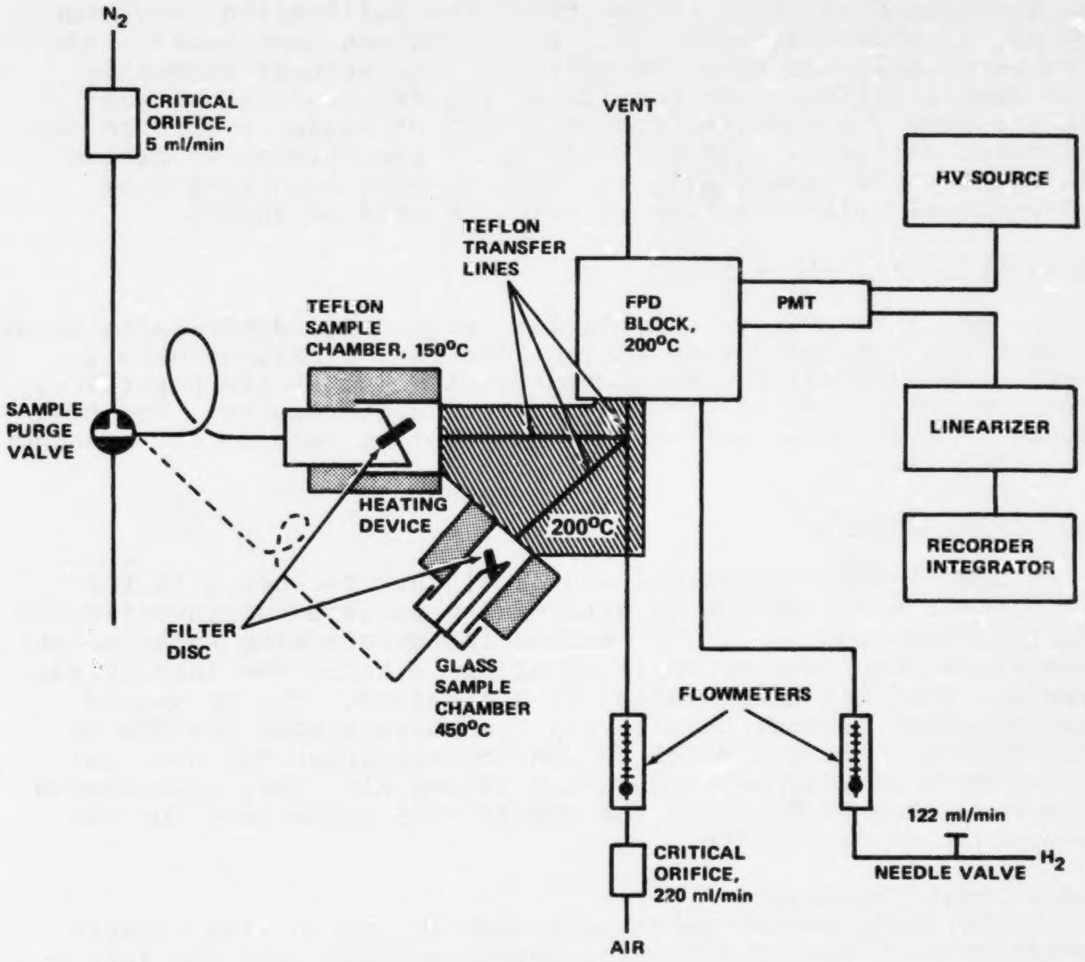
N_2
CRITICAL ORIFICE, 5 ml/min
VENT
HV SOURCE
TEFLON TRANSFER LINES
FPD BLOCK, 200°C
PMT
TEFLON SAMPLE CHAMBER, 150°C
SAMPLE PURGE VALVE
LINEARIZER
HEATING DEVICE
200°C
RECORDER INTEGRATOR
FILTER DISC
GLASS SAMPLE CHAMBER 450°C
FLOWMETERS
122 ml/min
H_2
NEEDLE VALVE
CRITICAL ORIFICE, 220 ml/min
AIR

Figure 9. Remodified flame photometric detector apparatus for H_2SO_4 and PDA-SO_4 analysis.

Calibration of the FPD with PDA-SO_4--

Following modifications of the FPD apparatus to allow volatilization at 450°C, calibration data were obtained for thermal decomposition of the perimidylammonium sulfate (PDA-SO_4) derivative of sulfuric acid. To obtain these data, standard solutions of sulfuric acid in isopropanol were added to Mitex filters impregnated with PDA-Br and the resulting derivative (PDA-SO_4) was decomposed at 450°C in the FPD. The calibration curve for PDA-SO_4 is shown in Figure 10. In subsequent experiments, samples were collected from the sulfuric acid aerosol generator with PDA-Br filters; the results of the FPD analyses of the filters gave the expected concentration of sulfuric acid in the generator effluent. The sensitivity of the derivative method was found to be essentially the same as that resulting from conventional volatilization of sulfuric acid at 200°C.

Barium Chloranilate Method

Use of the barium chloranilate method for determining total sulfate was limited during many of the derivatization experiments. The derivatization compounds used interfered positively with the BCA method by giving erroneous high results. The BCA method is also pH sensitive and could not be used in the presence of strong alkali.

Ion Chromatography

Due to the substantial degree of interference with the BCA method, a new method of determining sulfate was investigated. The ion chromatographic (IC) method for determining water soluble ions first described by Small *et al** eliminated the interference problems that had complicated the BCA method. The IC method also provided greater sensitivity for sulfate than the BCA or FPD methods. After a Model 10 Ion Chromatograph had been purchased from the Dionex Corporation (Sunnyvale, CA), experiments were conducted to optimize the operational parameters for the determination of sulfate.

Operational Parameters--

The instrumental parameters used in the initial experimentation with the IC for anion determinations were the following:

- Analytical column—3-mm i.d. by 500-mm anion separator.
- Suppressor column—6-mm i.d. by 250-mm anion suppressor.

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*Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Detection, *Anal. Chem.*, *47*1801-1809, 1975.

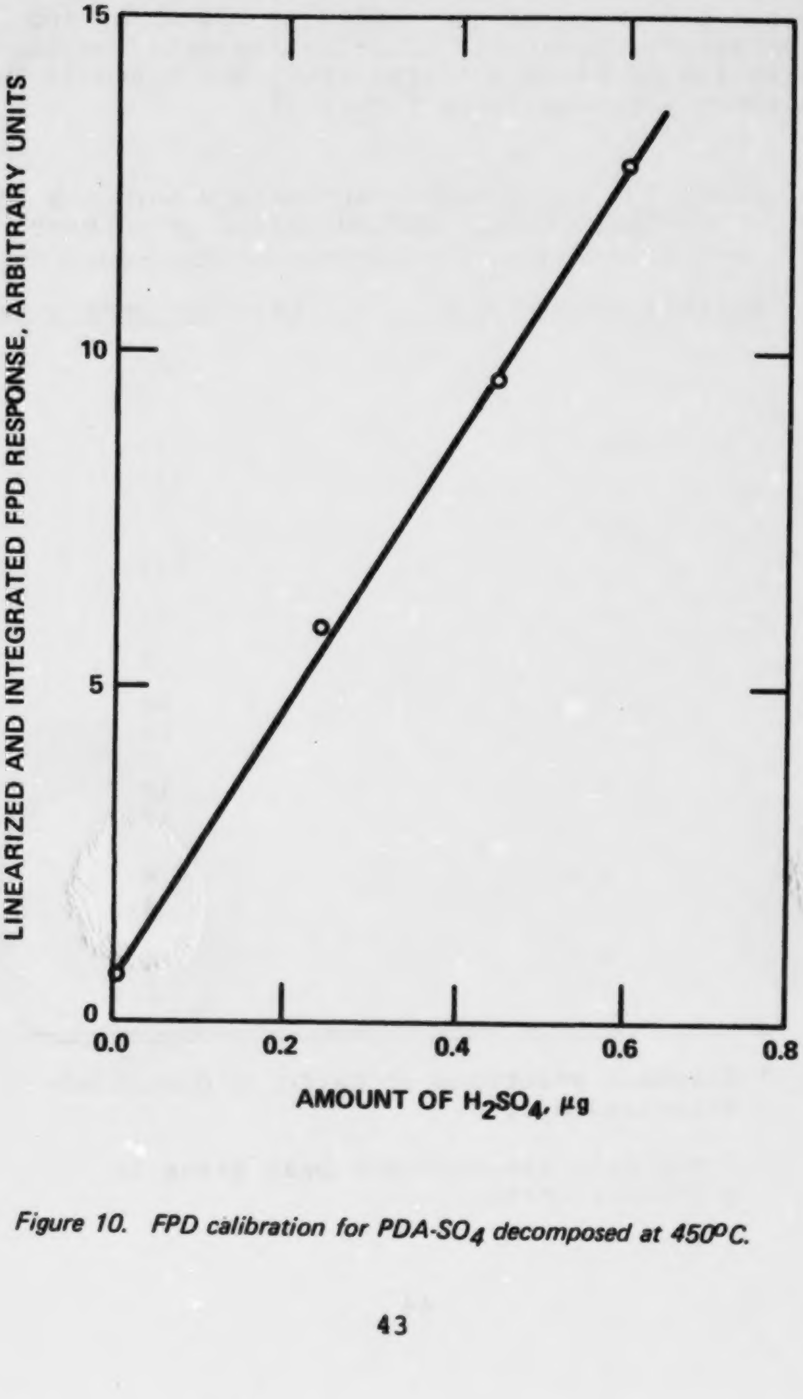

Figure 10. FPD calibration for PDA-SO_4 decomposed at 450°C.

- Eluent—0.003 M $NaHCO_3$/0.0024 M Na_2CO_3.
- Eluent flow rate—138 ml/hr.
- Sample volume—100-µl loop.

With these parameters the elution time for sulfate was approximately 14 min. This time was later reduced to 7 min by increasing the flow rate of the eluent to 230 ml/hr and keeping the other parameters constant. Calibration data for sulfate obtained with the parameters listed above are given in Table 13 and are shown graphically in Figure 11.

TABLE 13. PRELIMINARY CALIBRATION DATA FOR ION CHROMATOGRAPHIC DETERMINATION OF SULFATE

Sulfate taken,* ppm	Relative peak area†
338	650 655
169	310 315
68	111 110
34	51 51
17	28 28
6.8	10.7 10.7
3.4	4.1 4.3
0.7	1.1 1.2

* Standard solutions of Na_2SO_4 in distilled-deionized H_2O.

† These data are relative peak areas in arbitrary units.

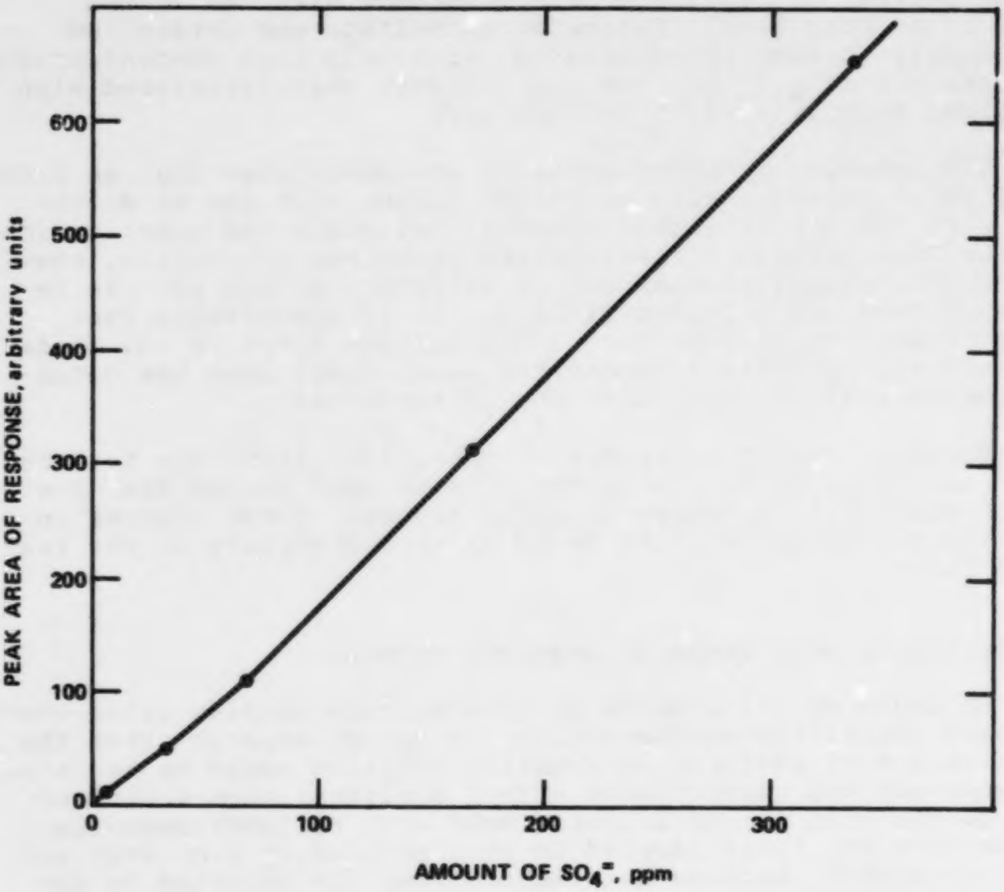

Figure 11. Ion chromatograph calibration with standard solutions of Na_2SO_4 in H_2O.

In order to minimize interferences from organic materials and suspended particulates in sulfate determinations and to extend the life of the analytical column, a precolumn supplied by Dionex was added to the IC. Also, the use of a shorter separator column to decrease the analysis time and a larger (500-µl) sample loop to increase the sensitivity for sulfate were investigated but proved impractical for our purposes.

With a relative standard deviation of less than 2%, the reproducibility of replicate determinations with the IC was judged to be very good. Furthermore, sulfate was determined successfully in samples containing relatively high concentrations of substances (e.g., chloride and nitrate) that interfered with analytical methods used in earlier work.

Disregarding interferences, it was calculated that as little as 0.1 µg of sulfuric acid per 47-mm filter disk can be determined with extraction with ultrasonic agitation and quantitation with the IC. Results of preliminary experiments indicate, however, that a significant amount of sulfate (ca. 0.5 µg) can be extracted from blank Teflon filters. It is conceivable that the magnitude and variability of the sulfate blank on the filter materials may ultimately impose the lower limit upon the determination of sulfuric acid with the IC technique.

Several sets of instrumental operating parameters for the determination of sulfate with the IC were used during the development of the final prototype sampling system. These changes in operating parameters will be noted where appropriate in the text that follows.

DERIVATIZATION WITH PERIMIDYLAMMONIUM BROMIDE

In light of the results of interference studies using conventional collection methodologies, it became apparent that the stabilization of sulfuric acid during sampling would be necessary. This approach was investigated with a derivatization technique based on the reaction of sulfuric acid with perimidylammonium bromide (PDA-Br) first adapted to this problem by P.W. West and his associates.* Because this methodology was reported by the authors in their early studies to be selective for sulfuric acid, the reaction was studied as a means for derivatization of sulfuric acid aerosol in our work.

With this methodology samples are collected on filters impregnated with PDA-Br. Ideally, only the sulfuric acid aerosol reacts with the PDA-Br salt to form the insoluble sulfate before the acid can be neutralized or otherwise destroyed by other reactions. For quantitation of the PDA derivative, PDA-SO_4 is decomposed at 450°C for FPD measurement of a volatilized sulfur species.

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* Thomas, R. L.; V. Dharmarajan, G. L. Lundquist, and P. W. West. Measurements of Sulfuric Acid Aerosol, Sulfur Trioxide, and the Total Sulfate Content of the Ambient Air. Anal. Chem. 48(4): 639-641, 1976.

With regard to the speed of the derivatization reaction, preliminary work indicated that the fixation process was very rapid. For example, when Mitex filters impregnated with PDA-Br were used to collect sulfuric acid aerosol and were quickly analyzed (within 1 min of sampling) by FPD with volatilization at either 200 or 450°C, the expected FPD response was obtained at 450°C, but no response was observed at 200°C. This result indicated that the sulfuric acid aerosol reacted quickly and completely to form the more refractory PDA-SO_4.

Interference from Ambient Particulate Material

In further experiments ambient particulate material was evaluated as a cause of interference in the derivatization process during sample collection. In these experiments, Mitex filters impregnated with the PDA-Br reagent and plain filters (not impregnated) were used to sample the ambient atmosphere. Determination of the derivatized sulfuric acid was performed with the FPD apparatus with decomposition of the derivative at 450°C. The results of these experiments are given in Table 14.

Approximately 100 µg of ambient particulate material (<2 µm) was collected on each filter. Known amounts of sulfuric acid aerosol from the generator were then deposited on the filters and analyzed by the FPD method with volatilization at 450°C. The amounts of sulfuric acid found were estimated from separate calibration curves (one for PDA-SO_4 and one for H_2SO_4). Because the slope of the calibration curve for sulfuric acid at 450°C is greater than for PDA-SO_4, it appeared that a given amount of acid yields a smaller FPD signal when it is converted to the PDA-SO_4 derivative.

Although earlier experiments had shown that an attenuated FPD response is obtained when nonimpregnated filters exposed to ambient particulate material and sulfuric acid are heated at 150 to 200°C, these results indicated complete recovery of sulfuric acid at 450°C (thermal decomposition of the reaction product of sulfuric acid and ambient particulate material). Complete recovery was also obtained from the PDA-impregnated filters. Thus it could not be concluded from these results that PDA-SO_4 was formed selectively in the presence of APM. The results merely showed that whatever the products of the reactions on the filters may be, the acid is recoverable from treated or untreated filters at 450°C, but not at lower temperatures. However, the smaller FPD responses for PDA-Br filters (see FPD responses listed in Table 14) were initially taken as a favorable indication that the

TABLE 14. DERIVATIZATION OF SULFURIC ACID AEROSOL WITH PDA-Br IN THE PRESENCE OF AMBIENT PARTICULATE MATERIAL

	H_2SO_4 aerosol added, μg*	Equivalent H_2SO_4 found, μg†	FPD response, arbitrary units§
Mitex filters impregnated with PDA-Br + APM#	None	6	75
	28	32	350
Plain Mitex filters + APM#	None	10	150
	32	36	600

* FPD analysis of the appropriate parallel filter exposed only to sulfuric acid aerosol served to determine the amount added.

† Each result is the average of triplicate determinations calculated from linearized integrated FPD responses. Relative standard deviation was typically less than ca. 10 to 20%. The FPD volatilization temperature was 450°C.

§ Separate calibration curves were prepared for impregnated filters.

# The amount of APM on each filter disk was about 100 μg (particle size, <2 μm).

PDA-SO_4 derivative may have been formed preferentially on the impregnated filters.

It should be pointed out that the ammonium sulfate salts present in APM would also contribute to the FPD response at 450°C regardless of whether they were fixed by the PDA-Br reagent or not. The contribution from sulfate salts in APM can be seen in the FPD responses listed in Table 14 for the filters to which no sulfuric acid aerosol was added. Also, the data for the filters with added sulfuric acid reflect this interference in that the analytical results for equivalent sulfuric acid exceeded the amount added.

On the other hand, if the sulfate salts were not fixed by the derivatizing reagent, it is possible that they could be selectively removed by volatilization at temperatures below the decomposition temperature of PDA-SO_4. Several experiments were conducted to investigate the possibility of prevolatilization of interfering sulfate salts, but the preliminary results were inconclusive. However, before proceeding further with this approach it was decided that the most important experiments were those that would establish whether or not the PDA-Br reagent fixed the ammonium salts of sulfuric acid.

Interference from Ammonium Sulfate Salts

Simultaneous fixation of ammonium sulfate salts and sulfuric acid constitutes a severe limitation on any methodology that depends upon selective derivatization of sulfuric acid aerosol. The selectivity of the PDA-Br reagent for sulfuric acid was evaluated in a relatively simple series of experiments with aerosols of ammonium bisulfate and ammonium sulfate.

Aerosols of these sulfate salts were collected simultaneously on plain and reagent-impregnated Mitex filters in a manner that was identical to experiments with sulfuric acid aerosols. The sulfate aerosols were generated in a laboratory apparatus by nebulizing dilute aqueous solutions of the appropriate ammonium salt with a Beckman No. 4020 atomizer-burner. This is the same device that is used for generation of the sulfuric acid aerosol; however, only argon (at a pressure of 140 kPa (20 psig)) was used to aspirate the feed solutions and the flame was not employed for generation of the sulfate salt aerosols.

In order to determine if the sulfate salts were fixed on the PDA-Br filters, FPD determinations were made on both plain and impregnated filters with a volatilization temperature of 200°C. At this temperature large FPD responses were observed for ammonium sulfate and ammonium bisulfate aerosols collected on plain Mitex filters. Thus, if the salts were not fixed on the PDA-Br filters, large FPD responses would be expected. On the other hand, if the sulfate salts were completely fixed and formed PDA-SO_4 in the same manner as sulfuric acid aerosol, then no FPD response would be observed at 200°C due to the higher decomposition temperature of the PDA-SO_4 derivative. The results of these experiments are shown in Table 15. These data indicate that both ammonium salts were partially fixed by topochemical reaction with PDA-Br. The estimated degree of fixation is about 80%. Thus, it was concluded that the reaction of PDA-Br to form the PDA-SO_4 derivative is not selective for sulfuric acid.

FIXATION OF SULFURIC ACID AEROSOL WITH VERSAPOR FILTERS

In earlier work at the Institute it was shown that sulfuric acid aerosol reacted with Versapor filters (Gelman Instrument Company) to form an insoluble product that could not be determined by methods depending upon extraction and that was probably

TABLE 15. EVALUATION OF SELECTIVITY OF PDA-Br WITH AEROSOLS OF SULFATE SALTS

	NH_4HSO_4 aerosol added, µg*	$(NH_4)_2SO_4$ aerosol added, µg*	FPD response, arbitrary units†,§	Sulfate derivatized, %
Mitex with PDA-Br	-	94	275	80
	81	-	250	95
Plain Mitex	-	94	1400	-
	81	-	4700	-

* The output of the aerosol generator was measured by determining sulfate with the barium chloranilate method and ammonium ion with the indophenol method.

† Volatilization temperature of the FPD apparatus was 200°C.

§ FPD responses were linearized and integrated.

a sulfate. The filter is characterized by the manufacturer as a glass-fiber medium with an epoxy binder.

In experiments with sulfuric acid aerosol it was found that the reaction product formed on Versapor filters was not decomposed to a volatile sulfur species at either 200 or 450°C. This result was evidenced by negligible FPD responses to filters exposed to sulfuric acid and analyzed in the FPD apparatus. Although not amenable to thermal volatilization-FPD analysis, the filter could be useful if it could be shown not to react with sulfate salts.

However, in experiments identical to those described in the previous section for PDA-Br filters it was demonstrated that the Versapor filters also fixed the ammonium sulfate salts as well as sulfuric acid by virtue of the fact that no FPD response was seen with the salts collected on these filters. Because Versapor filters did not appear to offer any advantage over PDA-Br impregnated filters for fixing sulfuric acid aerosol, work with these filters was discontinued.

SECTION 7

VOLATILIZATION, PREFILTRATION, AND DERIVATIZATION OF SULFURIC ACID AEROSOL

After it was demonstrated that PDA-Br filters fixed aerosols of sulfate salts as well as sulfuric acid aerosols, experiments were performed to determine if sulfuric acid aerosol could be volatilized during sampling and sulfates of lower volatility removed by filtration of the heated air stream.

PRELIMINARY APPARATUS WITH A SAMPLE FLOW RATE OF 3 L/MIN

To facilitate the thermal volatilization of sulfuric acid aerosol, a 30-cm section of 12-mm (i.d.) glass sampling probe was wrapped with a resistance heating tape. At a flow rate of 3 l/min, the aerosol sample from the laboratory generator could be heated in this manner from about 35°C to as high as 200°C. The sulfuric acid, thus vaporized, could be passed through a heated filter designed to remove particulate interferents and then onto a filter where fixation of the acid vapor could occur.

Passage of Sulfuric Acid through Sampling Probes and Filters

In preliminary experiments, the heated probe and a heated filter holder with a Mitex filter were run simultaneously with an identical reference sampling line that was not heated. The airstream was cooled in a 35-cm section of tubing following the filter. It then passed into an impinger-bubbler containing 80% isopropanol to collect vapors and recondensed sulfuric acid aerosol. Following the sampling period, any sulfuric acid condensed on internal surfaces behind the filters was rinsed into the bubblers. Because of the nature of the bubbler samples and the higher levels of sulfuric acid used in these preliminary experiments, it proved to be practical to use the barium chloranilate method for these analyses.

Preliminary results indicated that although only 30% of the total sample of sulfuric acid aerosol (relative to the reference side) could be accounted for, over 70% of this amount passed through the filter at 130°c. The recovery was only slightly increased by changing from a stainless steel filter holder to one constructed of Teflon.

These results suggested that the losses of sulfuric acid probably occurred in the heated zone of the glass sampling probe. This possibility was investigated further by determining the amount of sulfuric acid passing through the heated probe as a function of temperature. In these experiments the sulfuric acid was collected in impinger-bubblers following both the heated and reference probes. The results of these experiments are shown in Table 16. These data showed that for temperatures sufficient to volatilize an appreciable portion of the sulfuric acid aerosol (ca. 90 to 130°C), most of the resulting vapor was then lost to the walls of the heated glass probe.

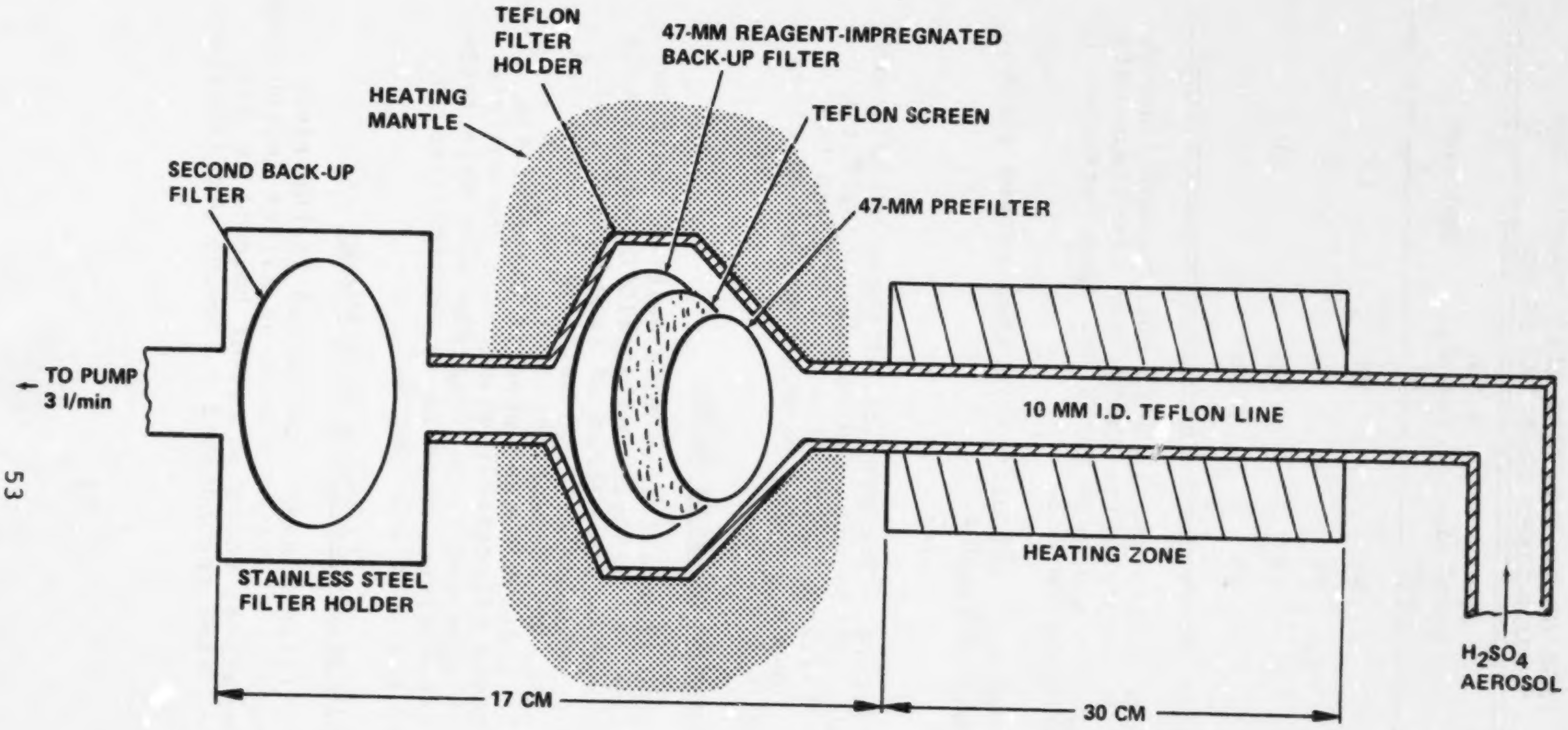
TABLE 16. PASSAGE OF SULFURIC ACID THROUGH THE HEATED GLASS SAMPLING PROBE

Temperature of heated sample airstream, °C	H_2SO_4 sampled, μg*	H_2SO_4 found, μg†	Recovery, %
76	122	129	106
82	106	108	102
84	103	105	102
108	111	68	61
129	117	31	26
133	100	29	29
200	115	33	29

* These are the amounts of sulfuric acid that passed through the unheated reference probe (ca. 30°C) run simultaneously with the heated probe. Analyses for H_2SO_4 were performed by the barium chloranilate method.

† These are the amounts of sulfuric acid that passed through the heated glass probe.

In an effort to improve the passage of sulfuric acid in the heated probe, a Teflon lining was inserted in the heated zone to reduce the reactivity of the inner surface. This thermal volatilization apparatus is shown schematically in Figure 12. An identical series of experiments was then performed to evaluate this modification. The results are given in Table 17. In contrast, these data showed that sulfuric acid vapor was passed efficiently through the heated zone with the Teflon lining. In further experiments with this apparatus the amount of sulfuric acid vapor passing through the Mitex prefilter was determined as a function of the



TEFLON
FILTER
HOLDER
47-MM REAGENT-IMPREGNATED
BACK-UP FILTER
HEATING
MANTLE
TEFLON SCREEN
SECOND BACK-UP
FILTER
47-MM PREFILTER
TO PUMP
3 l/min
10 MM I.D. TEFLON LINE
STAINLESS STEEL
FILTER HOLDER
HEATING ZONE
H_2SO_4
AEROSOL
17 CM
30 CM

Figure 12. *Apparatus for volatilization, prefiltration, and derivatization of sulfuric acid aerosol.*

TABLE 17. PASSAGE OF SULFURIC ACID THROUGH THE HEATED TEFLON-LINED SAMPLING PROBE

Temperature of heated sample airstream, °C	H_2SO_4 sampled, μg*	H_2SO_4 found, μg†	Recovery, %
82	90	96	107
102	78	71	91
184	69	56	81
204	47	35	75

* These are the amounts of sulfuric acid that passed through the unheated reference probe (ca. 30°C) run simultaneously with the heated probe; analyses for H_2SO_4 were performed by the barium chloranilate method.

† These are the amounts of sulfuric acid that passed through the heated Teflon-lined probe.

volatilization temperature. The results of these experiments are given in Table 18. These data indicated that sulfuric acid aerosol was volatilized efficiently at 110°C and that at least 90% of the resulting vapor passed the initial Mitex filter (heated to about 120°C).

Interference from Ammonium Sulfate Salts

After establishing that sulfuric acid aerosol could be efficiently volatilized and prefiltered at 110°C, experiments were conducted to determine the extent of interference, if any, from aerosols of ammonium sulfate salts under identical conditions. The results of these experiments are given in Table 19. These data indicated that prefiltration of the heated sample air stream effectively eliminated the sulfate salts. Therefore, it appeared to be feasible with this technique to eliminate interference from these particulates in the determination of sulfuric acid aerosol.

Derivatization of Sulfuric Acid Vapor with PDA-Br

In order to stabilize a sample collected in the field, we originally attempted the use of a back-up filter impregnated with PDA-Br (in a separate, unheated filter holder) to fix sulfuric acid aerosol that recondensed following prefiltration

TABLE 18. PASSAGE OF VOLATILIZED SULFURIC ACID AEROSOL THROUGH MITEX FILTERS AS A FUNCTION OF TEMPERATURE

Volatilization temperature, °C	Amount of H_2SO_4 aerosol sampled, μg*	H_2SO_4 found, μg on prefilter	H_2SO_4 found, μg passing prefilter†	Portion of H_2SO_4 passing prefilter, %
85	83	43	40	48
100	45	12	33	73
105	94	10	84	89
110	141	10	131	93

* The amount of aerosol sampled was determined with a parallel unheated sampling probe. All analyses for H_2SO_4 were performed by the barium chloranilate method.

† Sulfuric acid vapor passing the prefilter was determined with a back-up impinger-bubbler containing 80% isopropanol.

TABLE 19. RETENTION OF SULFATE SALT AEROSOLS BY A HEATED MITEX FILTER

Aerosol*	Amount sampled, μg†	Amount found, μg on prefilter	Amount found, μg passing prefilter§	Portion of salt retained, %
NH_4HSO_4	24	16	5	76
$(NH_4)_2SO_4$	48	45	<4	>90

* Temperature of the volatilization zone was 110°C.

† The amount of aerosol sampled was determined with a parallel unheated sampling probe. Analyses were performed by the barium chloranilate method for sulfate.

§ The amount of interferent slipping the prefilter was determined with a back-up filter followed by an impinger-bubbler containing 80% isopropanol.

of the vapor. However, in a series of experiments it was consistently observed that most of the vapor condensed on cool surfaces after prefiltration without forming an aerosol that could be collected on the impregnated filter. Therefore, it was of interest to determine if the vapor itself could be fixed by a PDA-Br filter. If so, the reagent-impregnated filter could be mounted behind the prefilter (with an appropriate spacer) in the same heated filter holder.

Accordingly, PDA-Br filters were used to sample sulfuric acid vapor at about 110°C and were analyzed by FPD to determine their retention of the vapor as PDA-SO_4. In these experiments it was found that less than 5% of the vapor was derivatized. These results suggested that any fixation reaction relying upon the formation of an insoluble sulfate derivative (e.g., PDA-SO_4 or $BaSO_4$) may not occur rapidly enough with sulfuric acid vapor to be useful. It appeared to be likely that the only suitable type of fixation scheme for sulfuric acid vapor would involve an acid-base reaction. Therefore, we began to evaluate the effectiveness of back-up filters impregnated with alkaline substances, such as Na_2CO_3 and NaOH, for reaction with the vapor at elevated temperatures. The preliminary results were favorable.

Derivatization of Volatilized Sulfuric Acid Aerosol with Alkali

After it was demonstrated that sulfuric acid vapor was not efficiently derivatized by filters impregnated with perimidylammonium bromide (PDA-Br), several experiments were conducted with Mitex filters impregnated with alkaline solids, such as sodium carbonate or sodium hydroxide. It was anticipated that the reaction of sulfuric acid vapor passing the prefilter would be very rapid on the back-up filter impregnated with the strongly alkaline material. Results of experiments in which sulfuric acid aerosol was sampled with the combined volatilization, prefiltration, and derivatization technique are given in Table 20. These data showed that sulfuric acid vapor was adequately fixed on Mitex filters impregnated with sodium hydroxide. A comparable level of sodium carbonate was somewhat less efficient in fixing the vapor. Although the alkali-impregnated filters were much more efficient than PDA-Br filters for derivatization of sulfuric acid vapor, a significant amount of the acid did slip the impregnated filters.

MODIFIED APPARATUS WITH A SAMPLE FLOW RATE OF 14-L/MIN

After it was established that sulfuric acid aerosol could be efficiently volatilized and then prefiltered at approximately 110°C and that more than 75% of interfering sulfate salts were removed by the prefilter after passage of the aerosols through the heated probe at temperatures as high as 130°C, modifications were made so that the sampling rate of the apparatus could be increased from 3 to 14 l/min to allow shorter collection periods for ambient levels of sulfuric acid aerosol.

TABLE 20. DERIVATIZATION EFFICIENCY OF ALKALI-IMPREGNATED FILTERS FOR SULFURIC ACID VAPOR AT 110°C

Impregnated alkali*	H_2SO_4 aerosol sampled, μg†	H_2SO_4 found, μg			Vapor collection efficiency of back-up filter, %#
		on prefilter	on impregnated back-up filter	slipping back-up filter§	
Na_2CO_3					
low level of impregnation	58	12	14	32	30
high level of impregnation	76	9	57	10	85
NaOH					
low level of impregnation	60	12	40	9	82
	53	<4	43	10	81
	106	23	66	17	80

* The alkali was impregnated onto Mitex filters from saturated alcoholic solutions.

† The amount of aerosol sampled was determined with a parallel, unheated sample probe. All analyses were performed by the barium chloranilate method for sulfate and reported as equivalent H_2SO_4.

§ Slippage was determined with a secondary back-up filter (reagent-impregnated) followed by an impinger-bubbler containing 80% isopropanol.

# The collection efficiency is relative to the amount of H_2SO_4 vapor to which the impregnated filter was actually exposed.

New Sampling Probe

A larger sampling probe was constructed from a 1.2-m by 12.5-mm i.d. brass outer tube with a longer 1.35-mm by 9-mm i.d. Teflon liner. Both ends of the Teflon tube were threaded so that filter holders or other devices could be attached directly. To effect the thermal volatilization of sulfuric acid aerosol, an 80-cm section of the Teflon-lined brass tube was wrapped with a resistance heating tape and then insulated. A thermocouple was attached to the surface of the probe to monitor the temperature of the heated zone so that overheating of the Teflon liner could be avoided. A second thermocouple was inserted into the Teflon filter holder behind the impregnated collection filter. This thermocouple was used to record the actual temperature of the heated airstream during sample collection.

To evaluate the modifications to the sampling apparatus, the heated probe (120°C) and the heated filter holder (130°C) were operated simultaneously with a reference sampling line that was not heated. Results of preliminary experiments with sulfuric acid aerosol are given in Table 21. These data indicated that an average of about 85% of the volatilized sulfuric acid successfully passed through the heated zone of the new probe. The data presented in Table 22 show further that an average of about 84% of the sulfuric acid vapor from the heated zone passed through the Mitex prefilter. On the basis of the data from both tables an overall efficiency of about 70% was indicated for the combined volatilization and prefiltration process. In earlier experiments the overall efficiency for the volatilization and prefiltration at a flow rate of 3 l/min was found to be in excess of 80%. Nevertheless, the modified sampling system appeared to be adequate.

Derivatization of Volatilized Sulfuric Acid Aerosol with Alkali at Increased Flow Rate

With regard to the fixation or derivatization of sulfuric acid on an alkali-impregnated filter (following the prefilter), preliminary results with the new probe, shown in Table 23, suggested that the efficiency was significantly lower at the increased flow rate. Low efficiency was indicated by slippage of a substantial portion of the acid vapor past the impregnated filter into a back-up impinger-bubbler. Initial efforts to improve the efficiency by increasing the level of impregnated alkali were only partially successful. Furthermore, interferences with the analytical method precluded conclusive evaluation of the effect of increased impregnation of alkali.

It appeared that the face velocity through the impregnated 47-mm filters may have been too great at the 14-l/min flow rate to allow efficient reaction of the acid vapors with the

TABLE 21. VOLATILIZATION EFFICIENCY OF THE HEATED PROBE AT A TEMPERATURE OF 120°C AND A FLOW RATE OF 14 l/MIN

Amount of H_2SO_4 aerosol sampled, μg*	Amount of H_2SO_4 found, μg†	Recovery %
152	130	86
141	125	89
143	99	70
117	112	96

* Determined by barium chloranilate analysis of the filter from the reference probe.

† Determined by barium chloranilate analysis of the impinger-bubbler catch following the heated probe.

TABLE 22. PREFILTRATION EFFICIENCY OF MITEX FILTERS AT A TEMPERATURE OF 130°C AND A FLOW RATE OF 14 l/MIN

Amount of H_2SO_4 vapor sampled, μg*	Amount of H_2SO_4 found, μg		Portion of H_2SO_4 passing prefilter, %
	on prefilter	passing prefilter†	
94	17	75	82
104	16	88	85

* This is the amount of volatilized sulfuric acid aerosol from the heated zone of the sampling probe. All H_2SO_4 analyses were performed by the barium chloranilate method.

† The sulfuric acid vapor that passed through the prefilter was determined by analysis of an alkali-impregnated filter and a back-up impinger-bubbler.

TABLE 23. EFFICIENCY OF SULFURIC ACID DERIVATIZATION BY ALKALI-IMPREGNATED TEFLON FILTERS AT A FLOW RATE OF 14 1/MIN

Amount of H_2SO_4 aerosol sampled, µg	Amount of H_2SO_4 found,* µg			Efficiency of impregnated filter, %
	on prefilter	on impregnated filter	passing impregnated filter	
29	8	9	12	43
104	16	28	60	32
60	20	<2	38	<5
50	13	25	12	68

* Determinations of sulfate were made by the barium chloranilate method. H_2SO_4 passing the impregnated filters was collected in an impinger-bubbler containing 80% isopropanol.

impregnated alkali. In other experiments it was found that higher volatilization temperatures (ca. 150°C) also decreased the efficiency of derivatization with the impregnated filters.

Because the higher flow rate is desirable for shorter sampling periods with ambient sulfuric acid aerosols, an effort was made to increase the efficiency by first increasing the level of impregnation of alkali and then by using thicker Teflon filters for impregnation. Unfortunately, evaluation of the results of these experiments was complicated by a substantial degree of interference with the barium chloranilate (BCA) method for sulfate. The interference was apparently due to increased levels of chloride that resulted from the neutralization with hydrochloric acid of excess alkali extracted from the impregnated filters. However, preliminary results based on BCA analyses of the back-up bubblers containing the isopropanol indicated that somewhat less sulfuric acid slipped the thicker alkali-impregnated filters.

To obtain a more meaningful evaluation of the modifications to the sampling system, it was necessary to develop a new method for determining sulfate extracted from the alkali-impregnated filters. The major problem was due to substantial interference with the barium chloranilate method that was previously used to measure sulfate fixed on the impregnated filters. Because of this interference problem, a study of the feasibility of determining derivatized sulfuric acid in a filter extract with ion chromatography (IC) was begun. In addition to offering greater sensitivity for sulfate than the BCA method, the IC method eliminated the interference problems that had complicated previous experiments.

Modified Extraction and Determination Procedures for Sulfate on Impregnated Filters

After operational parameters were established for the determination of sulfate with the IC, experiments were performed to study the extraction of sulfate from alkali-impregnated Teflon filters. In previous work with impregnated filters, isopropanol (IPA), rather than water, was used for extraction of sulfate due to the hydrophobic nature of Teflon. Although IPA readily wets the Teflon filters and efficiently extracts sulfate, an organic solvent was not expected to be compatible with direct analysis by IC. This conclusion was substantiated in a series of experiments in which sulfate was determined in aqueous solutions containing a small amount of IPA. These conditions approximated the process of initial wetting of the Teflon filter with a small volume of IPA and subsequent dissolution of the extracted sulfate and IPA with aqueous extraction. It was found, however, that solutions containing as little as 5% of IPA caused deleterious swelling of the ion-exchange resin in the analytical column of the IC.

In order to eliminate the need for an organic solvent to wet the filters, a method of aqueous extraction in which the Teflon filters are submerged in water in small vials was found to be very efficient when performed with ultrasonic agitation. However, because a substantial amount of excess NaOH was extracted from alkali-impregnated filters, only a limited number (ca. five) of sulfate determinations could be performed with the IC before it was necessary to regenerate the suppressor column. Neutralization of the excess alkali with HCl prior to analysis of the filter extracts appeared to extend the regeneration interval, although a problem was encountered with poor resolution of the resulting large chloride and small sulfate peaks. Subsequently, it was found that adequate resolution could be obtained with the use of two anion separator (analytical) columns in series. With a flow rate of 184 ml/hr and with 3-mm i.d. by 500-mm and 3-mm i.d. by 250-mm columns installed in the IC, a retention time of about 14 min was observed for sulfate. This arrangement facilitated IC determination of sulfate extracted with water from alkali-impregnated filters following neutralization of the excess alkali in the extracts.

Experiments were subsequently conducted to investigate the feasibility of direct analysis of the aqueous extract by IC without neutralization of the excess alkali. Therefore, several parameters were modified to eliminate the need for prior neutralization. The amount of KOH impregnated on each Teflon filter (temporarily used as a substitute for NaOH) was reduced by one-half to approximately 60 mg/filter. Also, the volume of water used for extraction was increased to 4 ml/filter. Theses changes effectively reduced the concentration of KOH present in the extract by 75%.

After the above changes had been made, calibration data for sulfate were generated with alkali-impregnated filters spiked with known amounts of standard sulfuric acid solutions. The spiked filters were extracted with water by ultrasonic agitation for 10 min in 4-ml glass vials sealed with Teflon-lined closures. The IC parameters used for analysis of these extracts were the following:

Analytical column--3 mm i.d. by 500-mm anion separator
Supressor column--6-mm i.d. by 250-mm anion suppressor
Eluent--0.003 $\underline{M}$ $NaHCO_3$/0.0024 $\underline{M}$ Na_2CO_3
Sample volume--100-µl loop

With these parameters, the elution time for sulfate was approximately 12 min.

Derivatization of Volatilized Sulfuric Acid Aerosol with Alkali at Increased Flow Rate as Measured by Ion Chromatography

After a quantitative method for the extraction and determination of sulfate from the alkali-impregnated filters had been established, experiments were continued in the evaluation of the combined volatilization, prefiltration, and derivatization methodology for sulfuric acid aerosol. Specifically, emphasis was placed on improving the efficiency of the alkali-impregnated Teflon filters for the collection of the volatilized sulfuric acid aerosol. As stated, previous evaluations of the efficiency of Teflon filters impregnated with large amounts (≈50 mg/ml) of NaOH for the collection of volatilized sulfuric acid were inconclusive.

In further experiments Mitex filters were replaced with a new Teflon filter purchased from Schleicher and Schuell (TE-35 disk-membrane). These filters consist of a Teflon membrane similar to Fluoropore supported by a coarse Teflon-fiber mat. In the current filter sequence for the combined sampling methodology, a Mitex prefilter is followed by a second Mitex filter that serves as a spacer. These filters precede the NaOH or KOH-impregnated TE-36 Teflon filter, which is oriented with the heavy felt-like side toward the airstream. Because the impregnated filter and spacer are in contact, both are extracted for the sulfate determination.

After calibration data were generated, sulfuric acid aerosol samples were collected by the combined volatilization, prefiltration, and derivatization methodology. Parallel samples were collected (including the unheated reference probe) at

14 l/min for 10 min with the temperature of the airstream of the heated probe maintained at about 110°C (measured behind the filter). In these experiments the heating mantle that was used previously for the filter holder was not needed to maintain the elevated temperature.

The results of these experiments are given in Table 24. These data indicated that an average of about 90% of the sulfuric acid aerosol that was sampled was found on the filter media (primarily on the impregnated filter with a small portion on the prefilter). Therefore, the slip through the impregnated filters could have been no more than 10% of the total sulfuric acid that was sampled. However, as suggested by previous experiments, the sulfuric acid that was not collected on the filters (i.e., 10%) was probably lost in the heated zone of the probe and never reached the prefilter or impregnated filter. These derivatization efficiency results can be compared to a value of 43% that was found earlier (Table 23) for the same sampling flow rate of 14 l/min. This increase in efficiency was probably due to the greater surface area and more effective level of impregnation afforded by the thicker felt-like Teflon filter (S & S TE-36).

TABLE 24. EFFICIENCY OF SAMPLING METHOD FOR SULFURIC ACID AEROSOL

Amount of H_2SO_4 aerosol added,* µg	Amount of H_2SO_4 found,† µg		Collection efficiency of impregnated filter,§ %	Portion of total H_2SO_4 on impregnated filter,# %
	On prefilter	On impregnated filter		
10.7	2.0	6.8	78	64
23.9	4.4	18.8	97	76
25.0	4.0	19.0	91	76
32.0	3.8	26.2	93	82
28.0	4.4	22.4	95	82
36.0	5.0	28.6	92	80

* The amount of aerosol added was determined with a parallel, unheated probe with an impregnated filter. All analyses were performed by IC.

† Samples were collected at 110°C at 14 l/min for 10 minutes.

§ The collection efficiency is based on the maximum amount of H_2SO_4 reaching the impregnated filters (e.g., [28.6/(36.0 - 5.0)] x 100% = 92%).

These figures relate the amount of H_2SO_4 found on the impregnated filter as compared to the total H_2SO_4 sampled (e.g., [28.6/36.0] x 100% = 80%).

SECTION 8

DEVELOPMENT OF PROTOTYPE SAMPLER FOR SULFURIC ACID AEROSOL

The sampling apparatus for sulfuric acid aerosol described at the conclusion of Section 7 was considered to have properties appropriate for its incorporation into a prototype sampler for sulfuric acid aerosol. It was realized, however, that steps would have to be taken to deal effectively with various sources of interference in the sampler. Thus, various interference studies as described below were undertaken in an effort to develop the changes in design that might be needed in the final design of the prototype sampler.

INTERFERENCE STUDIES

Studies were needed to determine the level of interference from gaseous copollutants that would not be removed by prefiltration. Sulfur oxide gases (specifically, sulfur dioxide) could be converted to sulfate by the alkali-impregnated filter. Basic gases such as ammonia could potentially react with the volatilized sulfuric acid aerosol to form sulfate salts which could be removed by the prefilter. Furthermore, APM collected on the prefilter might react with volatilized sulfuric acid and act as an additional cause of interference

Interference from Sulfur Dioxide

In the experiments with sulfur dioxide, the gas was introduced into the sampling probe with a syringe pump while room air was sampled under normal operating conditions of 110°C and 14 l/min. Determinations of sulfur dioxide were performed with the West-Gaeke method, in which Greenburg-Smith impingers containing the tetrachloromercurate reagent solution were placed in the sampling line after the impregnated filters. When a sulfur dioxide concentration of 75 $\mu g/m^3$ was sampled through the impregnated filters at either 25 or 110°C, about 75% of the sulfur dioxide was found in the back-up bubblers. The remaining 25% of the sulfur dioxide was collected on the impregnated filters, and when the filters were analyzed by IC, sulfate equivalent to a sulfuric acid aerosol concentration of 10 $\mu m/m^3$ was found.

Therefore, based on the results of these experiments, sulfur dioxide appeared to be a significant cause of interference with the method in its then-existing configuration.

The interference from sulfur dioxide was anticipated and two approaches that could possibly eliminate the problem were considered. One method involved low-temperature aqueous extraction of sulfate in the presence of sulfite on the impregnated collection filter. This method has been used successfully by other workers to demonstrate that very little sulfite exists with sulfate in ambient particulates. This approach depends, of course, upon sulfur dioxide reacting on the back-up filter to form sulfite with little or no oxidation to sulfate. However, because of the high alkalinity of the collection filter and the elevated temperature during sampling, sulfur dioxide collected on the impregnated filter was evidently converted to sulfate prior to extraction. Thus, this method was not promising.

The other method involved the use of an acid gas "denuder" to remove the sulfur dioxide prior to the thermal volatilization of the sulfuric acid aerosol. This denuder would simply be an extension of the existing sampling line to include a portion of tubing coated with an alkaline solid (e.g., NaOH). During sampling, acidic gases would quickly diffuse to the walls of the tubing and react with the alkaline material, eliminating the interference. Because sulfuric acid aerosol diffuses much more slowly, it would not react and would pass on to the collection device unattenuated.

Experiments were therefore conducted to evaluate the feasibility of using a gas diffusion denuder device in the sampling line for selective removal of sulfur dioxide. It was calculated from diffusion theory that at a flow rate of 14 l/min a single 5-mm i.d. by 800-cm tube coated with sufficient reactive alkaline material would remove more than 99.9% of the sulfur dioxide. However, for practical application of the gas diffusion denuder, a parallel arrangement of sixteen 5-mm i.d. by 50-cm tubes took the place of the single longer tube. This device is similar in concept to a denuder used by R.K. Stevens* and coworkers at the Environmental Protection Agency in Research Triangle Park, North Carolina, for removal of ammonia. The sampling apparatus, including the denuder, for the volatilization, prefiltration, and derivatization of sulfuric acid aerosol is shown schematically in Figure 13.

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*Stevens, R.K., T.G. Dzubay, G. Russworm, and D. Rickel. Sampling and Analysis of Atmospheric Sulfates and Related Species, Atmos. Environ., 12(1-3):55-68 (1978).

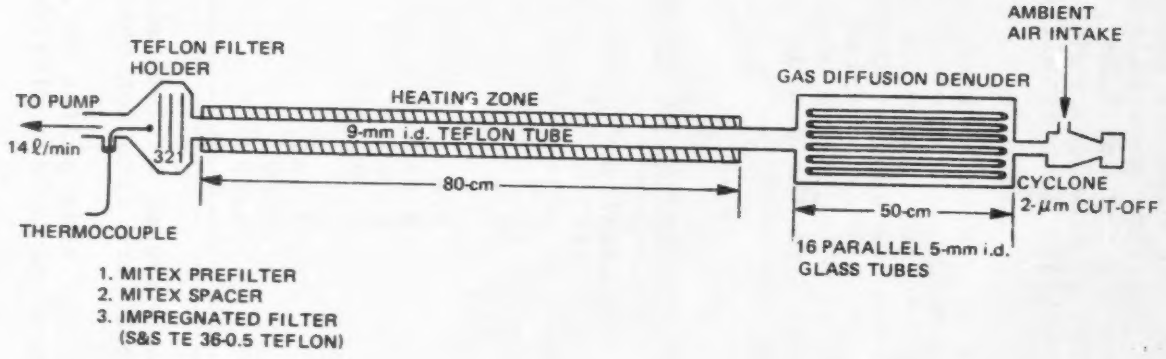
AMBIENT AIR INTAKE
TEFLON FILTER HOLDER
GAS DIFFUSION DENUDER
TO PUMP
HEATING ZONE
9-mm i.d. TEFLON TUBE
14 ℓ/min
3 2 1
80-cm
CYCLONE 2-μm CUT-OFF
50-cm
THERMOCOUPLE
16 PARALLEL 5-mm i.d. GLASS TUBES
1. MITEX PREFILTER
2. MITEX SPACER
3. IMPREGNATED FILTER (S&S TE 36-0.5 TEFLON)

Figure 13. *Apparatus for removal of interfering gases and volatilization, prefiltration, and derivatization of sulfuric acid aerosol.*

For evaluation of the effectiveness of the denuder, experiments were conducted with a single tube from the sixteen parallel tubes at an equivalent flow rate of 0.88 l/min. Sulfur dioxide was introduced into a mixing chamber with a syringe pump and diluted with room air. This mixture (sulfur dioxide concentration, 2.5 to 25 mg/m^3) was then sampled before and after passing through the denuder tube to determine the amount of sulfur dioxide removed by different alkaline materials coated from aqueous solutions onto the walls of the denuder tube. The effluent sulfur dioxide was collected in bubblers containing a 3% hydrogen peroxide solution and the sulfate that resulted was determined by ion chromatography.

The results of experiments with an uncoated denuder tube, one coated with sodium hydroxide, and another with sodium carbonate are shown in Table 25. Sulfuric acid aerosol (0.5 to 1 μm MMD) was also sampled through the denuder coated with sodium hydroxide to determine if any losses occurred. When a volume of aerosol containing 13.6 μg of sulfuric acid was sampled, the amount found in the effluent from the denuder tube was also 13.6 μg, indicating that no loss occurred.

TABLE 25. SULFUR DIOXIDE REMOVAL BY GAS DIFFUSION DENUDER

Denuder coating	SO_2 added,* mg/m^3	SO_2 passing denuder tube,* mg/m^3	SO_2 removal efficiency, %
None	23.7	23.7	0
	20.8	20.9	0
Na_2CO_3	15.7	0.3	98.2
	17.1	0.09	99.5
	19.1	0.08	99.6
	25.6	0.08	99.7
NaOH	2.5	<0.003†	>99.0
	7.9	<0.003†	>99.6
	23.5	<0.003†	>99.9

* Sulfur dioxide was measured by determination of sulfate in the peroxide bubblers with ion chromatography (IC).

† Limit of detection for this series of experiments was about 0.003 mg/m^3 of sulfur dioxide.

Thus, it was determined that the calculated efficiency for removal of sulfur dioxide (>99.9%) was obtained with the denuder coated with sodium hydroxide and that the sulfuric acid aerosol passed through this denuder with essentially no attenuation (100% recovery). The efficiency of a denuder coated with sodium carbonate was also measured because of the conversion of the hydroxide to carbonate that was expected to occur with ambient carbon dioxide. It was subsequently determined that conversion to carbonate would not cause a problem since the denuder coated with sodium carbonate operated with essentially the same efficiency (>99.5%) as the denuder coated with sodium hydroxide. Although these experiments were performed with inordinately large concentrations of sulfur dioxide, these results were taken as a favorable indication that the denuder would eliminate interference from ambient levels of sulfur dioxide.

Upon receipt of a gas diffusion denuder manufactured by University Research Glassware (Carrboro, N.C.), a method of coating the 16-parallel glass tubes was developed. A device was constructed to rotate the denuder while heated air was being drawn through the denuder to speed evaporation of the coating solutions. Sodium hydroxide was the substance applied for removing sulfur dioxide.

Experiments were conducted to determine the efficiency of the acid gas denuder for removal of sulfur dioxide. The results of these experiments are given in Table 26. Experiments were also conducted to determine the loss, if any, of sulfuric acid aerosol passing through the acid gas denuder. These data are given in Table 27. The results of the experiments with the acid gas denuder show that 99% of the sampled sulfur dioxide was removed while the sulfuric acid aerosol passed unattenuated.

TABLE 26. SULFUR DIOXIDE REMOVAL BY GAS DIFFUSION DENUDER

SO_2 added*,† mg/m^3	SO_2 passing denuder tube,* mg/m^3	SO_2 removal Efficiency, %
34.5	0.34	99.0
34.5	0.38	98.9

* Sulfur dioxide was measured by determination of sulfate in hydrogen peroxide (3%) bubblers with ion chromatography (IC).

† SO_2 was metered into a 14 l/min airstream with a syringe pump.

TABLE 27. PASSAGE OF SULFURIC ACID AEROSOL THROUGH GAS DIFFUSION DENUDER

H_2SO_4 aerosol added, µg*,†	H_2SO_4 aerosol passing denuder, µg†	H_2SO_4 attenuated by denuder, %
12.2	12.5	0
11.3	11.1	1

* Determined with parallel reference probe.

† Sulfuric acid aerosol was sampled at 14 l/min for ten minutes. All analyses were done by IC.

Denuder for Ammonia

Interference from ammonia and other basic gases was precluded by the use of a denuder for these gases as well as for sulfur dioxide. A gas diffusion denuder for basic gases similar to the one for sulfur dioxide was fabricated by coating the walls of a second denuder with phosphoric acid rather than sodium hydroxide. The ammonia denuder performed with similarly favorable efficiencies as the acid gas denuder.

Dehumidifier Ahead of the Denuders

Because sodium hydroxide is hygroscopic, the removal of some water vapor from the sampled airstream by the acid gas denuder was expected. However, during only a 1-hr sampling period, an amount of water vapor was removed from a cubic meter of ambient air (relative humidity greater than 85%) that was sufficient to wash more than half the coatings from both the sodium hydroxide and phosphoric acid-coated denuders. To eliminate this problem, a method of dehumidifying the sampled airstream prior to passing through the denuders was developed.

The diffusion dehumidifier consists of an 11.5-cm i.d. by 80-cm clear acrylic tube mounted coaxially with a 20-mm i.d. by 80-cm porous stainless steel tube. The space between the two tubes is filled with approximately 5 kg of an indicating silica gel desiccant. The porous center tube allows the aerosol to pass through the dehumidifier while the water vapor diffuses into the silica gel, where it is adsorbed. The original silica gel desiccant functioned efficiently without needing to be replaced or regenerated after 50 hr of operation.

No measurements were made to determine the actual reduction in the humidity of the sampled airstream after passing through the dehumidifier, but the reduction was sufficient to eliminate the buildup of water in the denuders while sampling at relative humidities greater than 95%. On the other hand, experiments were conducted to determine the loss of sulfuric acid aerosol, if any, upon its passing through the dehumidifier. The results of these experiments are given in Table 28. These data show that the quantity of sulfuric acid aerosol was unattenuated by the dehumidifier.

TABLE 28. PASSAGE OF SULFURIC ACID AEROSOL THROUGH THE DEHUMIDIFIER

H_2SO_4 aerosol added, μg*,†	H_2SO_4 aerosol passing dehumidifier, μg†	H_2SO_4 aerosol passing dehumidifier, %
175.6	171.1	98
124.5	129.1	104
200.0	180.0	90
108.5	109.0	100
120.4	121.6	101

* Determined with parallel reference probe.

† Sulfuric acid aerosol was sampled at 14 l/min for 15 min. All analyses were done by ion chromatography.

Interference from APM

Experiments were also conducted to investigate the possibility of interference from APM deposited on the prefilter during sampling. Size-fractionated APM (<2 μm) was collected for 1 hr through a cyclone onto two Mitex filters in parallel lines. A Teflon overlay was used with each filter during sampling so that the APM was deposited on only one-half of each filter. With this arrangement of two parallel half-filters and a combined flow rate of 14 l/min, a face velocity was maintained through each filter that was consistent with normal collection conditions.

Laboratory generated sulfuric acid aerosol was then sampled at 14 l/min and 120°C using the Mitex prefilters preloaded with APM. Because half of each filter was clean or unexposed, each filter served as its own reference. Each prefilter and the corresponding impregnated filter were then cut in half and analyzed individually for sulfate by IC. The results of these experiments are given in Table 29. These data indicate that the relatively

TABLE 29. STUDY OF INTERFERENCE FROM AMBIENT PARTICULATE MATERIAL

Run	Type prefilter used	H_2SO_4 found on impregnated filter, µg
1	Unexposed	92.0
	APM preloaded	88.2
2	Unexposed	34.4
	APM preloaded	37.2
3	Unexposed	45.6
	APM preloaded	46.2

small amount of sized-fractionated APM deposited on the prefilter during the maximum 1-hr sampling period did not interfere significantly with the determination of sulfuric acid aerosol.

ASSEMBLY OF THE PROTOTYPE SAMPLING APPARATUS

After the feasibility of the combined volatilization, prefiltration, and derivatization methodology together with the removal of gaseous interferents using gas diffusion denuders had been demonstrated, a prototype sampler was constructed. The prototype sampler is shown schematically in Figure 14. The prototype sampler is mounted on an aluminum flex-frame lattice attached to a 2-m tall open-type relay rack. Casters added to both the bottom and side of the support rack allow the apparatus to be moved easily in either a vertical or horizontal position. A photograph of the complete prototype sampler and supporting framework is shown in Figure 15.

When the apparatus is in use, ambient air enters via a 3.2-mm i.d. stainless steel tube covered with a weather cap. (The sample is collected 1-m above ground level.) The sample is then passed through a cyclone to remove all atmospheric particulate matter (APM) larger than 2 µm in diameter. This lowers the buildup of APM on the prefilter during sampling. After the humidity is lowered in the dehumidifier, the sample passes through the two gas diffusion denuders. The denuders are shown in Figure 16. The first denuder is coated with phosphoric acid for re-

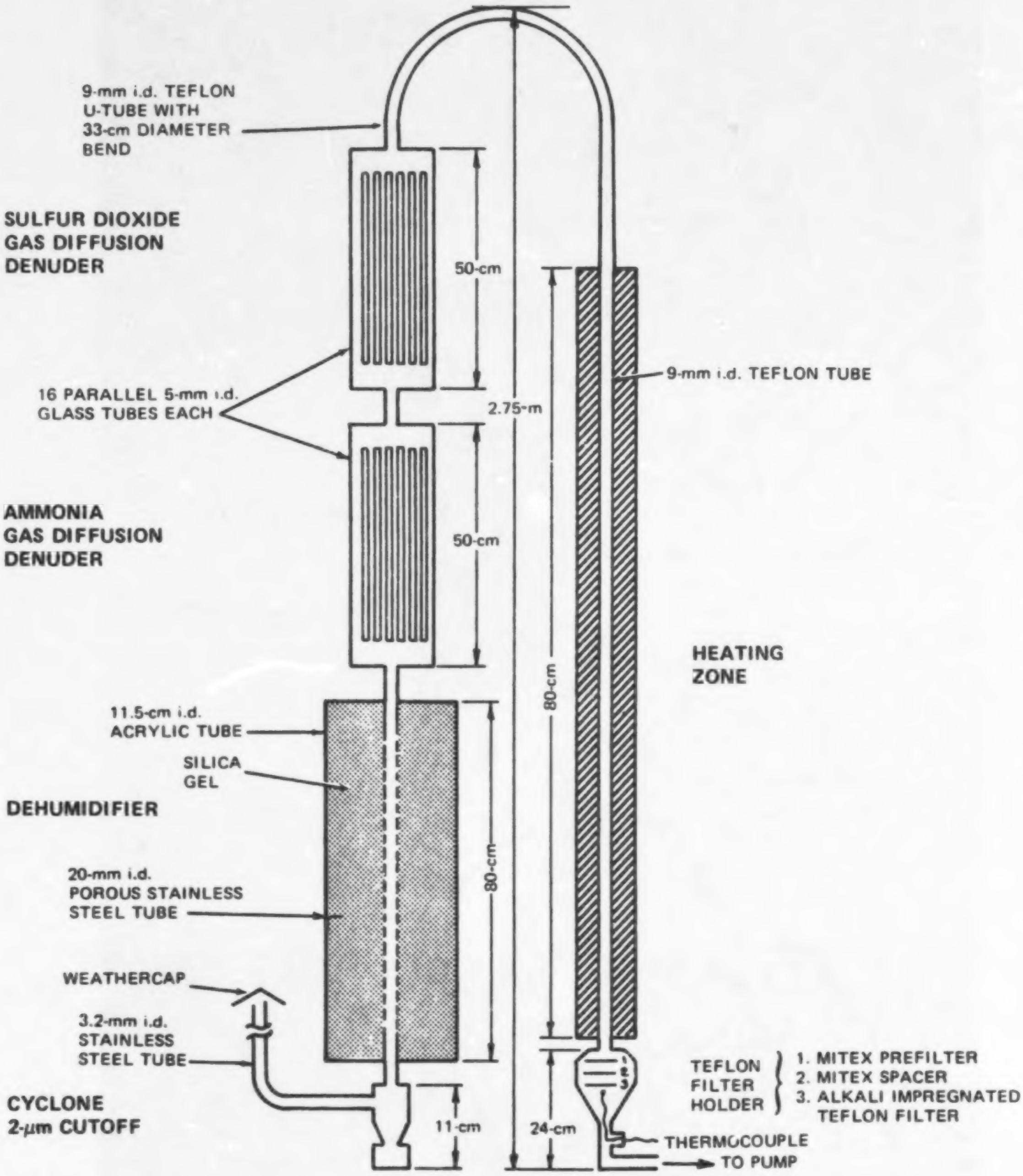
9-mm i.d. TEFLON U-TUBE WITH 33-cm DIAMETER BEND
SULFUR DIOXIDE GAS DIFFUSION DENUDER
50-cm
16 PARALLEL 5-mm i.d. GLASS TUBES EACH
2.75-m
9-mm i.d. TEFLON TUBE
AMMONIA GAS DIFFUSION DENUDER
50-cm
HEATING ZONE
80-cm
11.5-cm i.d. ACRYLIC TUBE
SILICA GEL
DEHUMIDIFIER
80-cm
20-mm i.d. POROUS STAINLESS STEEL TUBE
WEATHERCAP
3.2-mm i.d. STAINLESS STEEL TUBE
CYCLONE 2-µm CUTOFF
11-cm
24-cm
TEFLON FILTER HOLDER
1. MITEX PREFILTER
2. MITEX SPACER
3. ALKALI IMPREGNATED TEFLON FILTER
THERMOCOUPLE
TO PUMP

Figure 14. Apparatus for the removal of basic and acid interfering gases and the volatilization, prefiltration, and derivatization of sulfuric acid aerosol.

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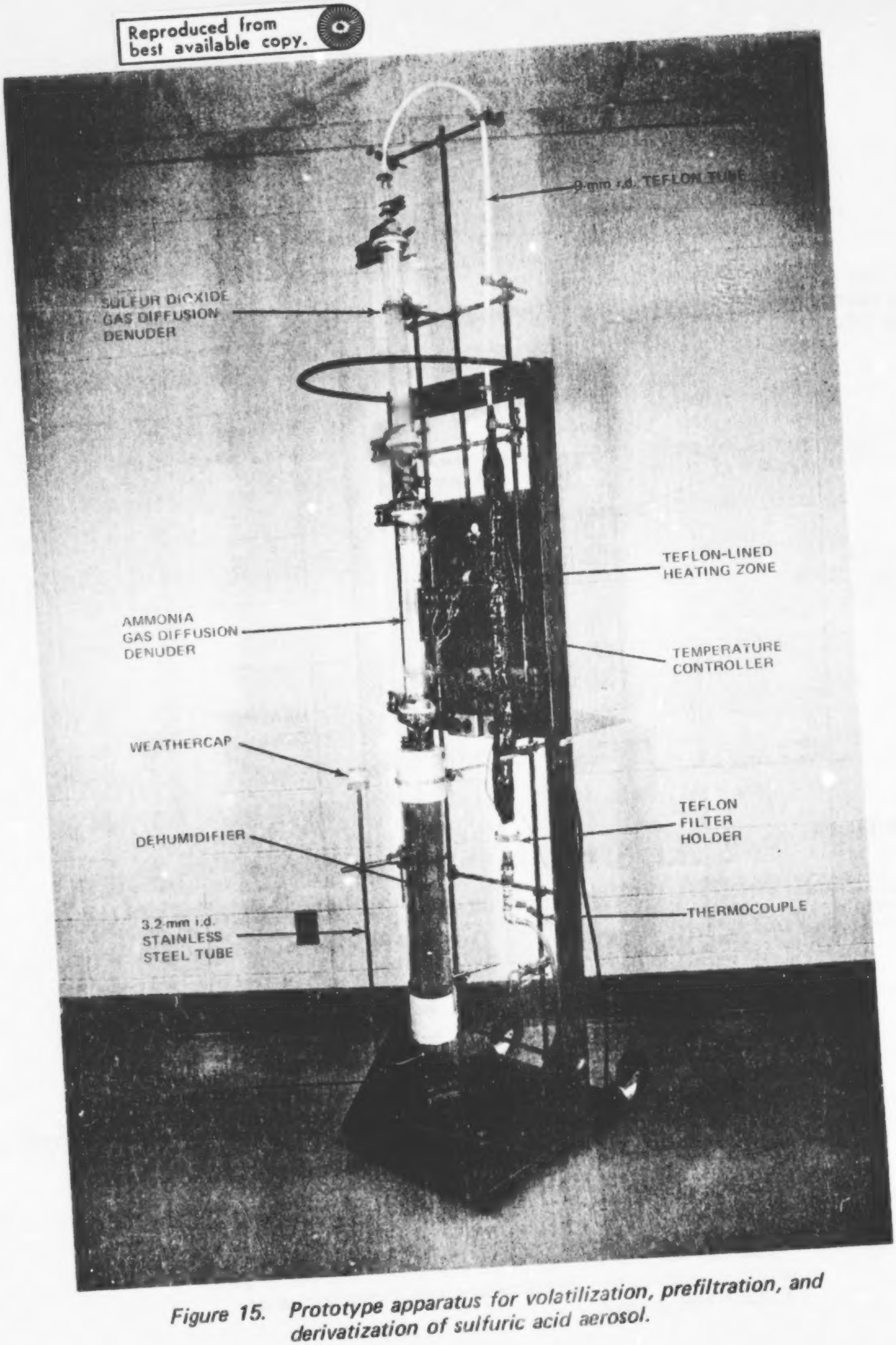
9-mm i.d. TEFLON TUBE
SULFUR DIOXIDE GAS DIFFUSION DENUDER
TEFLON-LINED HEATING ZONE
AMMONIA GAS DIFFUSION DENUDER
TEMPERATURE CONTROLLER
WEATHERCAP
TEFLON FILTER HOLDER
DEHUMIDIFIER
THERMOCOUPLE
3.2-mm i.d. STAINLESS STEEL TUBE

Figure 15. Prototype apparatus for volatilization, prefiltration, and derivatization of sulfuric acid aerosol.

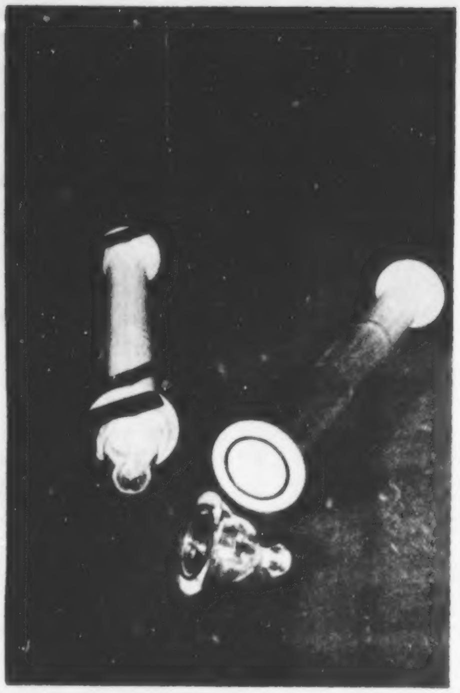

Figure 16. Gas diffusion denuders.

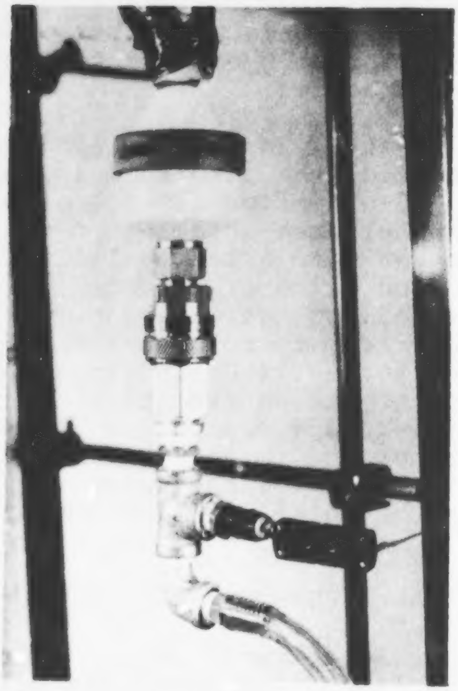

Figure 17. Teflon filter holder.

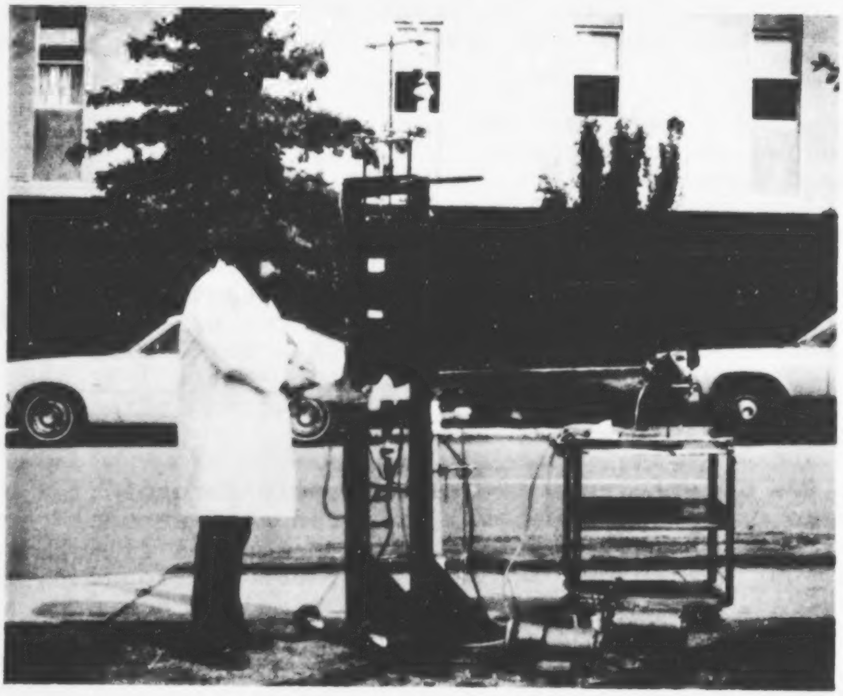

Figure 18. Ambient roadsite sampling with prototype sampling system.

moving ammonia and other alkaline gases, and the second is coated with sodium hydroxide for removing sulfur dioxide and other acidic gases.

After the larger APM and gaseous interferents have been removed, the airstream is then heated to 130°C in the 9-mm i.d. by 80-cm Teflon-lined heating zone. The heated sample in which the sulfuric acid aerosol has been selectively volatilized then passes into a Teflon filter holder containing a series of three Teflon filters. The Teflon filter holder is shown in Figure 17 and schematically in Figure 19. The first filter is a Mitex prefilter to collect the APM and unvolatilized sulfate salts. The third filter is the alkali-impregnated Teflon fiber-membrane filter for derivatizing the sulfuric acid vapor. The middle filter is a separating filter to keep the alkali from the prefilter and is analyzed with the impregnated filter. A thermocouple is located below the collection filter to allow regulation of the volatilization temperature at the point of collection.

FINAL LABORATORY EVALUATION OF PROTOTYPE SAMPLING SYSTEM

Experiments were conducted in which the concentration of the laboratory-generated sulfuric acid aerosol sampled by the prototype sampling system was gradually reduced toward anticipated ambient levels. Four concentration levels of sulfuric acid aerosol were generated; the average amounts sampled for the different levels were 121, 55, 19, and 7.4 μg/filter. The collection times for the different levels were 5, 10, 15 and 20 min, respectively. The results of these experiments are given in Table 30.

These data show that the percentage of sulfuric acid aerosol collected on the impregnated filter and the percentage of sulfuric acid aerosol collected on both filters increased as the amount of aerosol sampled was decreased. This apparent increase in sampling efficiency is probably due to the increase in sampling time rather than the amount of sulfuric acid aerosol sampled. Each sampling interval requires a short equilibration period to stabilize the volatilization temperature at 130°C. As the sampling time is increased from 5 to 20 min, the equilibration period becomes less significant. At a 1-hr sampling time for ambient samples, this initial warmup effect should become insignificant.

At the lowest level of sulfuric acid aerosol (7.4 μg/filter), an average of 83% of the total sulfuric acid aerosol sampled was collected on the prefilter and impregnated filter. Of the total amount collected, an average of 86% was found on the impregnated filter. However, these results are based on a laboratory generated sample concentration of 26 $\mu g/m^3$. Better results

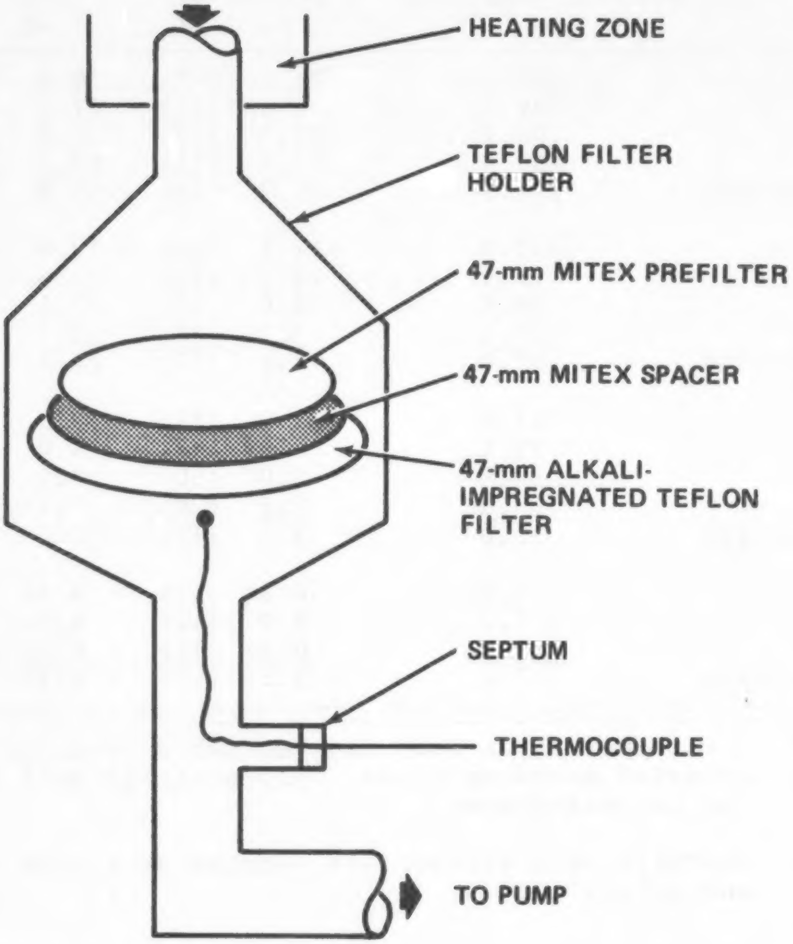
HEATING ZONE
TEFLON FILTER HOLDER
47-mm MITEX PREFILTER
47-mm MITEX SPACER
47-mm ALKALI-IMPREGNATED TEFLON FILTER
SEPTUM
THERMOCOUPLE
TO PUMP

Figure 19. Schematic of Teflon filter holder containing the Teflon prefilter and the alkali-impregnated Teflon collection filter.

TABLE 30. EFFICIENCY OF PROTOTYPE SAMPLING APPARATUS FOR VARIOUS CONCENTRATIONS OF SULFURIC ACID AEROSOL

	Amount of H_2SO_4 aerosol sampled,* µg	Amount of H_2SO_4 found,† µg (% of total H_2SO_4)		Portion of total H_2SO_4 collected, %
		On prefilter, µg (%)	On impregnated filter, µg (%)	
	120.3	21.7 (17)	59.4 (49)	67
	109.1	22.4 (21)	47.0 (43)	64
	101.7	27.2 (27)	34.3 (34)	61
	152.4	46.3 (31)	65.1 (43)	74
Average	120.9	29.4 (24)	51.5 (42)	66
	33.5	11.9 (36)	18.0 (54)	90
	76.9	14.9 (19)	31.4 (41)	60
	54.6	3.6 (7)	27.1 (50)	57
	55.1	3.2 (6)	30.0 (55)	61
Average	55.0	8.4 (17)	26.6 (50)	67
	17.4	1.9 (11)	9.9 (57)	68
	23.8	0.65 (3)	19.8 (83)	86
	19.6	5.8 (30)	7.1 (36)	66
	15.0	2.7 (24)	7.1 (47)	71
Average	19.0	3.0 (17)	11.0 (56)	73
	7.0	0.84 (12)	5.40 (77)	89
	7.2	0.87 (12)	6.05 (84)	96
	8.0	0.85 (11)	4.10 (54)	65
Average	7.4	0.85 (12)	5.18 (72)	84

* The amount of aerosol sampled was determined with a parallel, unheated sampling probe. All analyses were performed by ion chromatography.

† Sulfuric acid aerosol was sampled at a flow rate of 14 l/min and volatilized at 130°C.

may be obtained when the lower ambient levels that are anticipated are sampled. The minimum detectable level of the prototype sampling system appears to be approximately 0.5 µg/m^3.

SECTION 9

FIELD EVALUATION OF PROTOTYPE SAMPLER FOR SULFURIC ACID AEROSOL

After the laboratory experiments were completed, ambient sampling was done with the prototype sampler at two local roadside sites in the Birmingham, Alabama, area. A series of 1-hr samples were first collected for 6 days beside a city street during the period from August 6 to August 18, 1978. The sampler is shown at this location in Figure 18 on page 100. The average traffic flow during sampling was approximately 600 cars per hr. The sampler was located approximately 3 m from the street. Two control samples were collected with each sample to determine the amount of total sulfate and sulfate aerosol less than 2 μm in diameter present at the sampling site. The control data are reasonably consistent with the data obtained from the prototype sampling system. The data from these samplings are listed in Table 31. A graphic comparison of the amount of total sulfate and sulfuric acid aerosol present beside the city street is shown in Figure 20. Approximately 20% of the nonsized sulfate collected beside the city street was found to be sulfuric acid aerosol. The average amounts of total ambient sulfate and ambient sulfuric acid aerosol collected were 1.5 and 0.3 μg/m^3, respectively.

After the sampling beside the city street was completed, a field test was conducted next to a major highway. The prototype sampling system was set up in a parking deck adjacent to an elevated (8 m) six-lane interstate highway on the north side of Birmingham, Alabama. The prototype sampler is shown collecting samples at the interstate highway site in Figure 21. The samples were collected 8 m from the near side and 1.5 m above the interstate highway. The angle of the incline from the center of the interstate highway to the sampling system was approximately 5°. Samples of 1-hr duration were collected for 12 hr on August 21, 22, and 23, 1978. On these dates the local atmospheric particulate counts were 94, 108, and 97 μg/m^3, respectively, with a temperature low of 21°C and a high of 34.5°C on each of the test dates. On August 21 and 23 there was a slight breeze of 3 to 5 km/hr crossing the interstate highway toward the sampling system. On August 22, however, the wind direction

TABLE 31. AMBIENT SULFURIC ACID AEROSOL DETERMINATIONS BESIDE A CITY STREET

Date collected	Time started	Prototype samples*			Control samples*	
		$SO_4^=$ found on prefilter, µg/m^3	H_2SO_4 found on impregnated filter,† µg/m^3	Total $SO_4^=$ found on prefilter and impregnated filter, µg/m^3	Total $SO_4^=$ less than 2-µm diameter,§ µg/m^3	Total $SO_4^=$,# µg/m^3
8-9-78	9:30	0.32	0.23	0.55	0.29	0.14
	10:30	0.11	0.19	0.30	0.26	0.11
	11:30	0.41	0.07	0.48	0.68	0.16
8-14-78	8:30	0.89	4.12	5.01	1.49	3.71
	9:30	1.20	0.40	1.60	1.19	3.82
	10:30	0.90	0.90	1.80	1.69	7.64
	11:30	1.41	1.70	3.11	3.07	8.10
	12:30	0.55	1.80	2.36	0.39	0.63
	1:30	0.60	2.31	2.91	0.64	1.39
8-15-78	8:30	0.36	0.14	0.50	0.57	0.71
	9:30	0.40	0.28	0.68	0.63	0.89
	10:30	0.49	0.19	0.68	0.63	0.99
	11:30	0.45	0.15	0.50	0.52	1.07
	12:30	0.54	0.10	0.64	0.63	0.83
	1:30	0.54	0.22	0.76	0.72	0.94
	2:30	0.81	0.10	0.91	0.74	0.81
8-16-78	8:30	0.64	0.00	0.64	0.64	0.48
	9:30	0.32	0.00	0.32	0.48	0.79
	10:30	0.79	0.00	0.79	0.95	1.43
	11:30	0.64	0.24	0.88	0.64	0.64
	12:30	0.48	0.00	0.48	0.48	0.48
	1:30	0.00	0.00	0.00	0.00	0.32
8-17-78	9:30	1.27	0.00	1.27	1.11	1.59
	10:30	1.11	0.00	1.11	1.11	1.27
	11:30	0.64	0.48	1.12	0.95	2.54
	12:30	2.06	0.00	2.06	1.27	1.27
	1:30	0.79	0.00	0.79	0.79	0.64
	2:30	0.48	0.00	0.48	0.64	1.11
8-18-78	9:30	0.64	0.00	0.64	0.64	0.95
	10:30	0.32	0.00	0.32	0.32	1.11
	11:30	0.79	1.29	2.08	2.06	2.86
	12:30	0.48	0.16	0.64	0.64	0.64
	1:30	0.79	0.00	0.79	0.79	1.90

---

* All analyses by ion chromatography.

† Volatilization temperature was 130°C. All sampling was done at a flow rate of 14 l/min.

§ Determined with separate control filter with a 2-µm diameter cutoff cyclone.

# Determined with separate open-face filter.

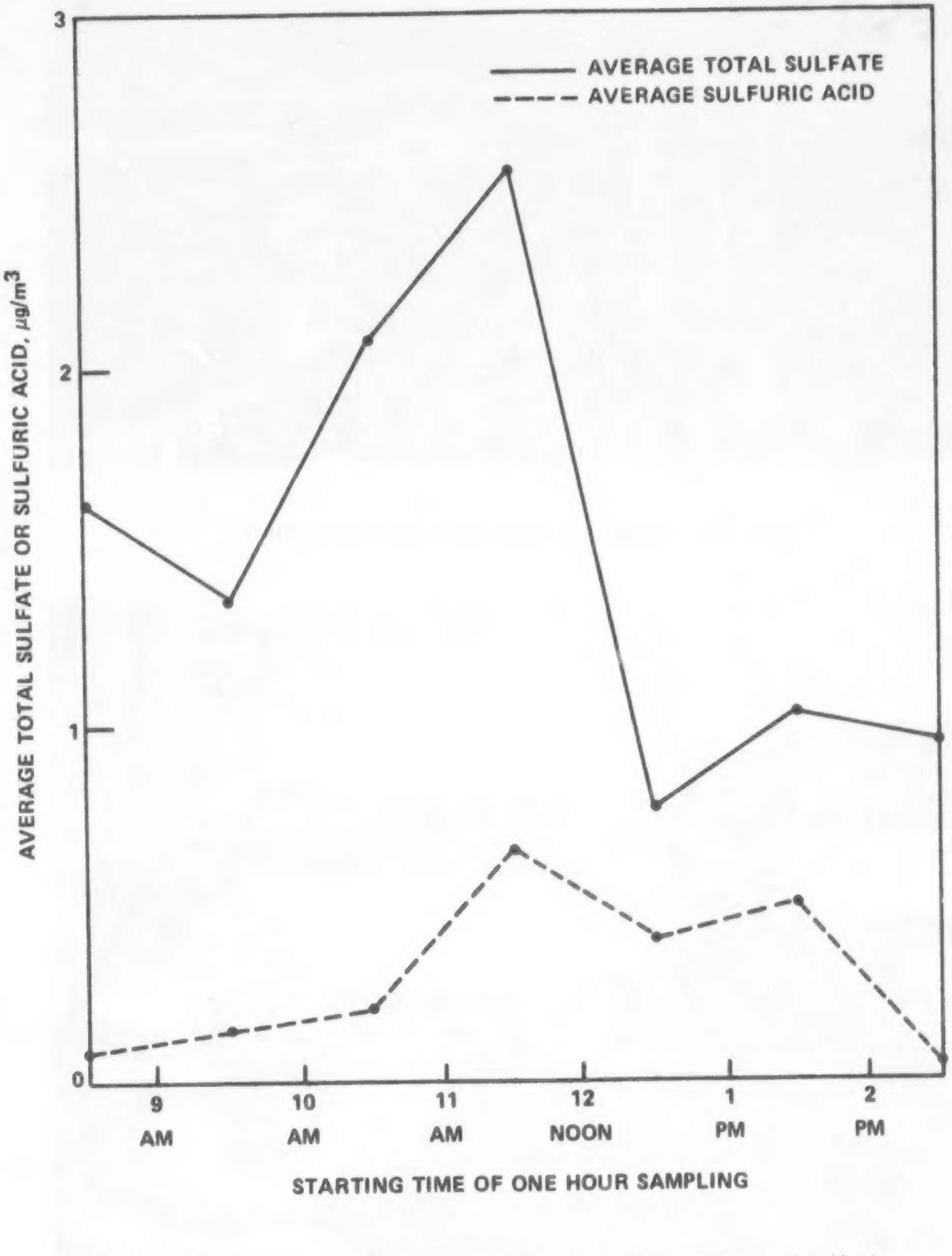

Figure 20. Hourly average concentrations of total sulfate and sulfuric acid on six days beside a city street.

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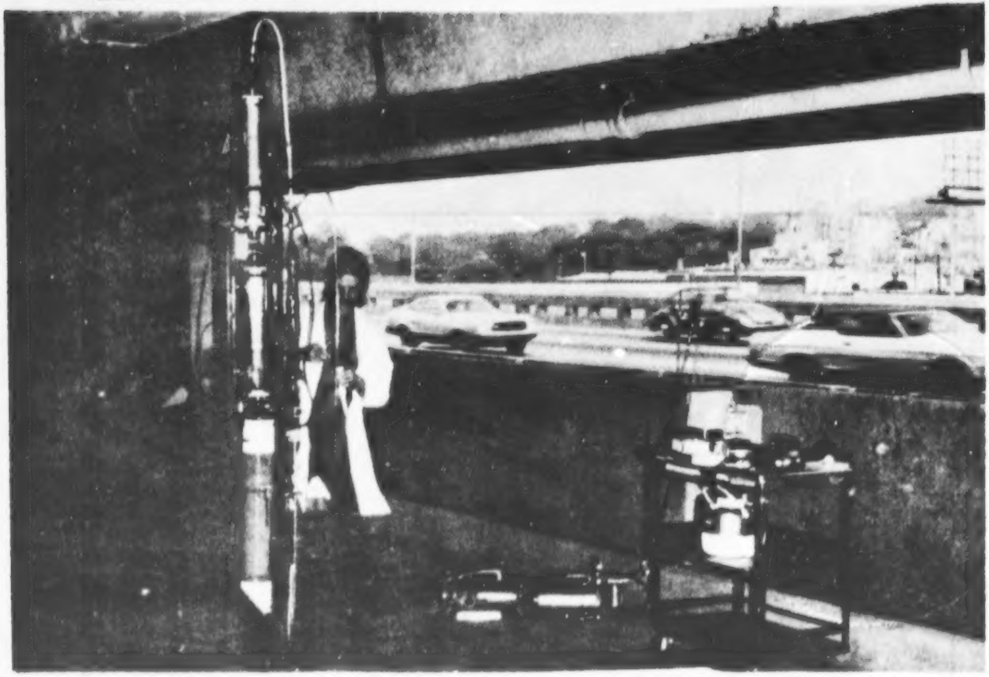

Figure 21. Remote sampling at interstate highway.

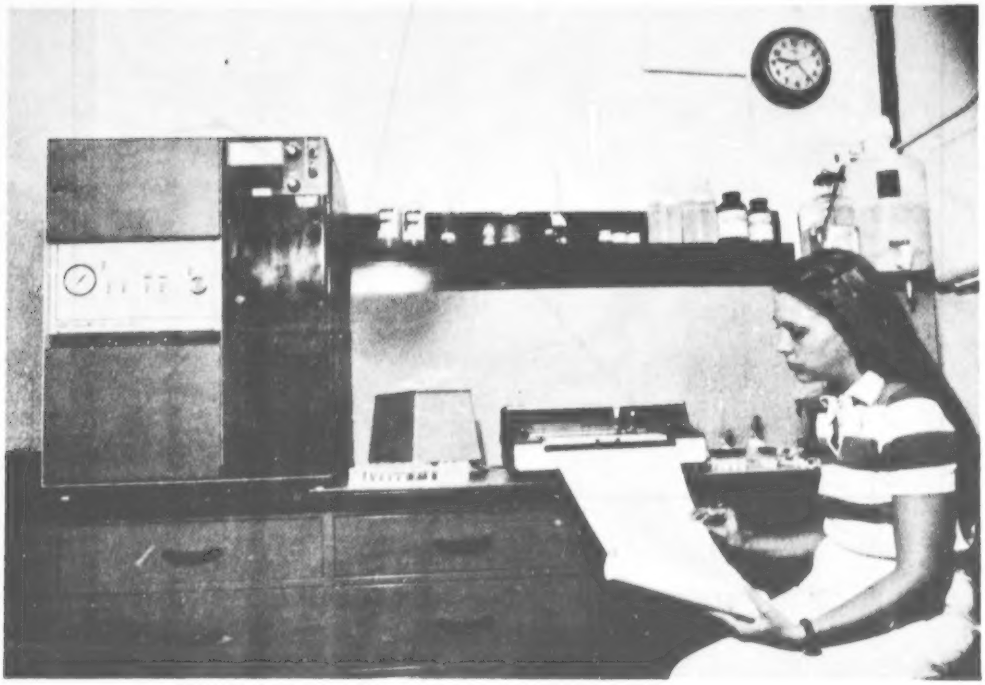

Figure 22. Ion chromatographic analyses of collected samples.

and velocity were variable during most of the sampling period. The average traffic flow passing the sampling site as determined from government traffic counts was approximately 8,000 to 10,000 cars per hour.

As before, two control samples were collected with each sulfuric acid aerosol sample. All samples collected were brought back to the laboratory in individual glass vials for analysis by IC (Figure 22.) The data from these samplings are given in Table 32. Figure 23 shows a graphic comparison of the concentrations of total sulfate and sulfuric acid aerosols collected hourly on August 23, 1978, at the interstate highway. Figure 24 is a graphic comparison of the average concentrations of total sulfate and sulfuric acid aerosols by time of day collected from the 3 days of field testing at the interstate highway location. Approximately 30% of the nonsized sulfate collected beside the interstate highway was found to be sulfuric acid aerosol. The average amounts of total ambient sulfate and ambient sulfuric acid aerosol collected were 4.4 and 1.4 μg/m^3, respectively.

TABLE 32. AMBIENT SULFURIC ACID AEROSOL DETERMINATIONS FROM REMOTE INTERSTATE HIGHWAY SAMPLING

		Prototype samples*			Control samples*	
Date collected	Time started	SO$_4^=$ found on prefilter, μg/m	H$_2$SO$_4$ found on impregnated filter,[†] μg/m	Total SO$_4^=$ found on prefilter and impregnated filter, μg/m	Total SO$_4^=$ less than 2-μm diameter,[§] μg/m	Total SO$_4^=$,[‡] μg/m
8-21-78	6:00	1.46	3.10	4.56	4.37	5.95
	7:00	1.72	4.29	6.01	6.22	10.32
	8:00	1.32	0.71	2.03	2.12	3.04
	9:00	1.85	3.33	5.18	5.03	7.04
	10:00	0.93	0.00	0.93	0.93	1.06
	11:00	0.66	1.91	2.57	2.65	5.03
	12:00	0.79	2.38	3.17	2.91	5.95
	1:00	1.06	3.10	4.16	4.10	5.82
	2:00	1.06	1.67	2.73	0.53	1.98
	3:00	0.93	1.19	2.11	2.12	0.79
	4:00	1.19	1.90	3.09	3.31	2.65
	5:00	0.79	1.19	1.98	1.98	0.93
8-22-78	6:00	0.79	1.43	2.22	2.06	14.29
	7:00	0.48	1.43	1.91	1.90	3.02
	8:00	1.11	1.43	2.53	2.43	3.90
	9:00	0.64	1.43	2.07	2.22	6.98
	10:00	0.48	3.57	4.05	0.48	0.64
	11:00	0.56	3.10	3.66	0.48	2.54
	12:00	0.64	0.00	0.64	0.79	1.27
	1:00	0.64	2.70	3.34	0.32	0.48
	2:00	0.48	0.32	0.80	0.79	0.79
	3:00	0.48	0.00	0.48	0.48	0.48
	4:00	0.48	2.70	3.18	0.48	0.48
	5:00	0.64	1.58	2.22	2.06	3.02
8-23-78	6:00	0.64	0.00	0.64	0.48	0.64
	7:00	0.95	0.00	0.95	0.64	0.32
	8:00	1.27	0.00	1.27	1.27	2.06
	9:00	1.43	3.57	5.00	5.24	6.35
	10:00	0.64	1.67	2.31	2.38	5.08
	11:00	0.95	0.00	0.95	0.95	2.22
	12:00	0.64	2.38	3.02	3.02	4.44
	1:00	0.64	0.00	0.64	0.64	2.54
	2:00	0.48	0.00	2.38	2.38	3.65
	3:00	2.06	1.90	2.06	1.94	8.41
	4:00	1.27	0.00	1.27	1.27	2.38
	5:00	0.64	0.00	0.64	0.64	3.02

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* All analyses by ion chromatography.

[†] Volatilization temperature was 130°C. All sampling was done at a flow rate of 14 l/min.

[§] Determined with separate control filter with a 2-μm diameter cutoff cyclone.

[‡] Determined with separate open-face filter.

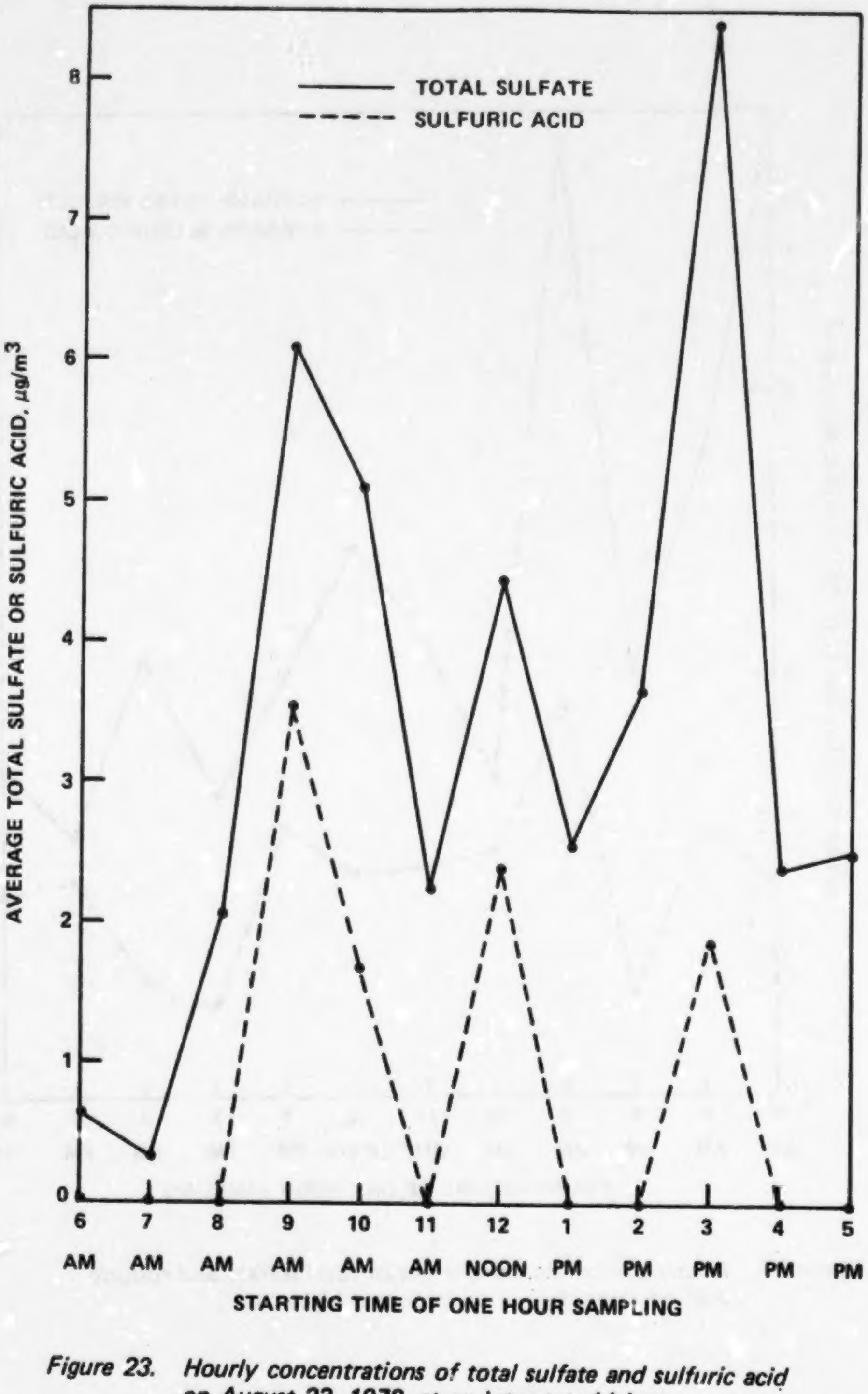

Figure 23. Hourly concentrations of total sulfate and sulfuric acid on August 23, 1978, at an interstate highway.

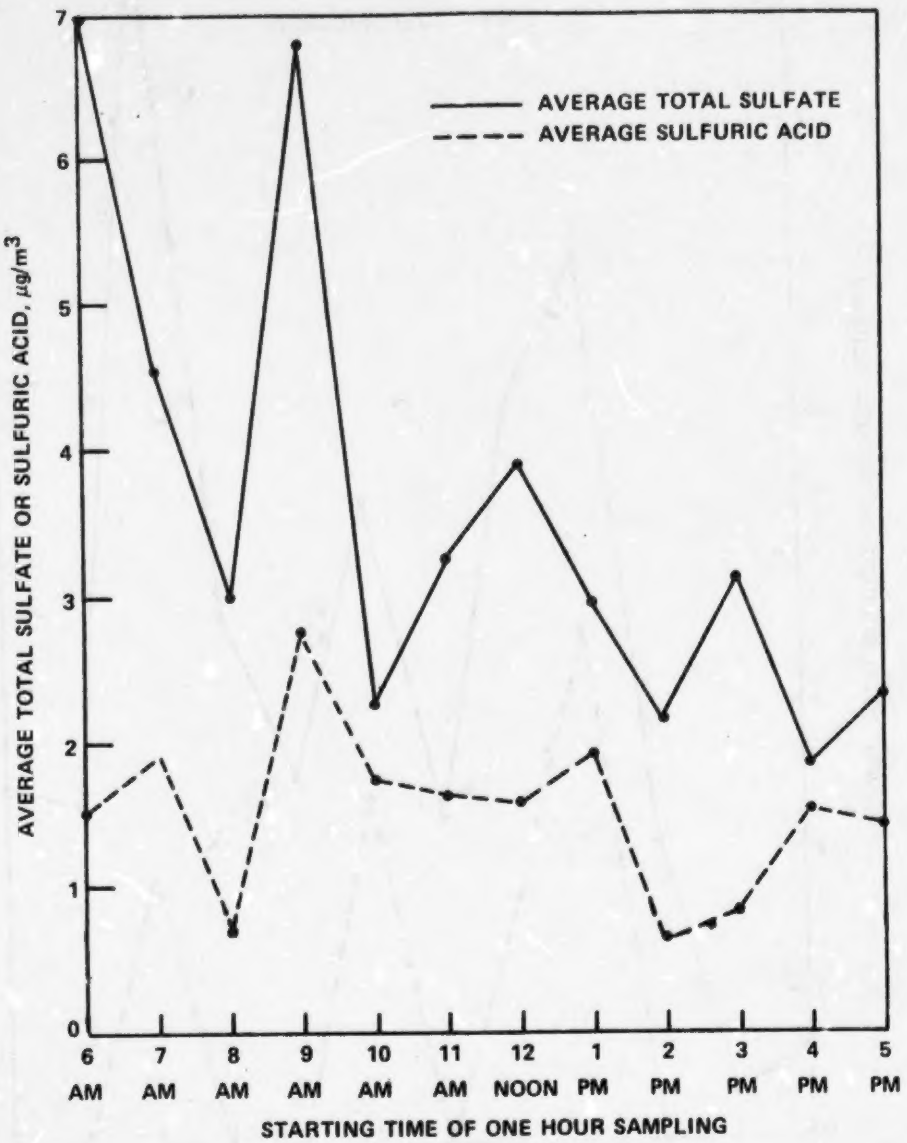

Figure 24. Hourly average concentrations of total sulfate and sulfuric acid on three days at an interstate highway.